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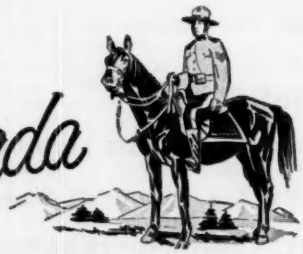

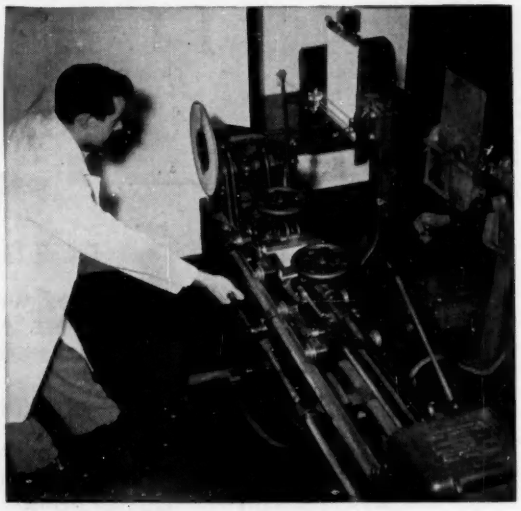

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The Supercontraction of Wool in Solutions of Lithium Salts

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Abstract

The supercontraction of various types of wool, modified wool, and other keratins has been studied using concentrated solutions of lithium salts, particularly the bromide. The purity of the lithium bromide has been found to be of considerable importance, traces of bromine in the solution having a profound effect. With bromine concentrations in the range 10^{-4}–10^{-5} *M*, marked differences between clean and detergent-treated wools have been observed. Removal of the bromine by means of thiosulfate has enabled quantitative measurements to be made of such variables as concentration of lithium bromide, time and temperature of treatment, etc.

I. Introduction

One of the unique properties of wool is its ability to undergo supercontraction, which may be defined as a spontaneous decrease in fiber length, reversible in some cases and irreversible in others. Determination of supercontraction has become an important method of measuring changes that have taken place by the modification of wool proteins. It may be induced by steaming a stretched wool fiber for short periods of time (less than 2 min.) and then relaxing the fiber in steam [5]. The various chemical reagents which bring about supercontraction may be divided into two main classes—those which are believed to split the disulfide bond, such as $NaHSO_3$ and Na_2S [30, 32], and those which are believed to break hydrogen bonds, such as lithium bromide and phenol [3, 4, 8, 14, 15, 28]. Beauregard et al. [7] have shown that wool will still supercontract in a reagent capable of breaking hydrogen bonds even after the disulfide bonds have been stabilized by conversion to bis-thio-ethers.

This work was begun with the intention of evaluating the relative importance of the above two types of linkages to the supercontraction process. However, from preliminary experiments with a reagent believed to break hydrogen bonds, namely lithium bromide [26], certain of the published results could not be reproduced [3, 4]. Hence, the reaction of wool with lithium salt solutions, in particular the bromide, has been studied in detail to elucidate the cause of this discrepancy. The nature and importance of impurities which appear to affect the

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supercontraction behavior have also been investigated.

II. Materials and Methods

Staples of Australian crossbred wool, 54's quality, from which the weathered tips had been removed, were used. They were cleaned by washing in petroleum ether and then water, Soxhlet extracting with absolute ethanol, followed by similar extraction with diethyl ether. After subsequent washing in many changes of double distilled water during several days, they were allowed to dry in air before storage in an all-glass container. The cleaned wool was not touched by hand after the alcohol stage. Where pen grown Lincoln 40's has been used, this is mentioned specifically. Human hair and horse hair (mane) were cleaned as above. Deaminated [31], esterified [17], and isoelectric [24] wools were also used.

Lithium salts from different manufacturers have been designated Sample A, Sample B, etc., and the subscript numbers (Sample A_1, Sample A_2) indicate different batches from the one maker. These salts were either of unspecified quality or met the requirements listed in the British Pharmaceutical Codex, 1934. The activated charcoal was an unknown grade of "norite." Analytical grade potassium hydrogen phthalate and recrystallized borax were used to prepare buffer solutions of pH 4 and pH 9, respectively.

The detergents used were (*a*) anionic: sodium lauryl sulphate (Du Pont) which, according to its odor, contained alcoholic impurities, (*b*) cationic: cetyl trimethyl ammonium bromide (C.T.A.B.), which was analytically pure and used as a primary standard, (*c*) nonionic: Triton X-100, a *p*-tertiary-octyl-phenyl-ethylene oxide adduct which was the purest available.

Solutions of LiBr (x %) were made by dissolving x g. salt in 100 ml. water (distilled), and then filtering when cold. They had a pH approximately 6 (pHydrion papers). Where the salt has been made in the laboratory, the B.P.C. method [9] was used, the HBr being first redistilled. The actual percentage LiBr present was determined as the bromide by the Mohr titration.

The ultraviolet spectra of the lithium salt solutions were examined in the range 240–400 mμ, using a 1-cm. cell in a Cary Recording Spectrophotometer 11MS. When small quantities of the respective halogen were added to the lithium halide solutions, the amount of available halogen present in the resulting solution was determined by titration with 0.005 N sodium thiosulfate solution, using starch-iodide indicator. The concentration of bromine in solutions too dilute to give a coloration with this indicator, was determined spectroscopically by optical density measurements at about 273 mμ.

For determination of surface active impurities in the LiBr, 1 ml. LiBr solution was spread on the surface of saturated $(NH_4)_2SO_4$ solution in a film balance. Any resulting film was then compressed to an area of about 40 sq. cm. and the surface pressure measured. Surface tensions were measured directly on a du Noüy tensiometer.

The detergents and dyes were adsorbed by treating wool (1 g.) with detergent solution (100 ml.) in glass-stoppered bottles, with intermittent shaking, at room temperature. After the required time, the detergent was decanted, its volume measured, and the wool washed with distilled water (100 ml.) to detect any desorption. The amount of detergent presumed to be retained was calculated from the difference between the initial and final detergent concentrations. (No corrections were made for the moisture content of the wool, the amount of water adsorbed by the wool from the solution, etc.)

The detergent concentrations were determined by the following methods: (*a*) *Anionic detergent:* The concentration of sodium lauryl sulfate was estimated volumetrically by titration with C.T.A.B. using the method suggested by Barr et al. [6], which was found to be satisfactory over the range of 0.00004–0.01 M. (The Epton method [16] is not satisfactory over such a large range.) (*b*) *Cationic detergent:* C.T.A.B. was analyzed by the procedure in (*a*). It was found preferable to titrate always with the cationic detergent. (*c*) *Nonionic detergent:* Since several attempts to develop a volumetric method for the analysis of this detergent, Triton X-100, were unsuccessful, the gravimetric method of Shaffer and Critchfield [29], as developed by Oliver and Preston [27], was used.

The surface active dye was purified via the barium salt to remove NaCl, and dye concentrations were measured spectrophotometrically at 490 mμ.

Supercontraction procedure. The ends of individual fibers (selected at random from a sample) were held between tweezers, one in each hand. The fiber was laid along a centimeter ruler graduated in millimeters, and extended until the crimp was just

removed. Lengths of 10 cm. (*i.e.*, ca. 0.1 mg. in weight) were then cut off and placed in separate stoppered tubes each containing about 2 ml. LiBr solution. The tubes and contents were heated in an air oven at 100° C. for 3 hr. unless otherwise specified. The fibers were thus free to move and coil at random. After the required time of heating, the fibers were removed from the solution by means of tweezers, then washed for 1 min. in boiling buffer solution, the length remeasured, and the percentage supercontraction calculated. Length measured by the above method [34] could be estimated to ± 2 mm. or within 4% on a 10-cm. fiber. When a fiber is stretched until the crimp is just removed [12], errors in tension have little effect on apparent length. Therefore contractions [3] of 4% might indicate very little or no contraction. The figures presented are the arithmetic means of the contractions of at least 10 fibers.

Diameter measurements were made at a magnification of 625 at 10 approximately equal intervals along a 10-cm. fiber. It was not possible to measure diameter at exactly the same points along the fiber before and after contraction. Volume changes were calculated from the length and diameter of individual fibers (regarded as cylinders) and are recorded as the arithmetic mean with the standard error of each mean.

III. Results

The changes in length (l), radius (r), and volume (v) after treating wool with 100% LiBr (Sample A_1) solution at 100° C. for 3 hr. are recorded in Table I.

Under these conditions it appears that crossbred wool contracts about 50% with a corresponding increase in diameter and negligible volume change. After similar treatment, Lincoln wool contracts 36%. In both cases, the contraction is unaffected by the pH of the after treatment (cf. [4]).

Alexander [4] has commented on the necessity to remove "deleterious impurity" from the LiBr solution. Since the salt used here and in his work was of commercial grade and since it cannot readily be purified by the usual methods of recrystallization (due to its high solubility), the nature and significance of the impurities were investigated. Surface active impurities were detected by the film balance and surface tension measurements, and the significance of these materials is reported in the next section. However, when other supplies of LiBr (Sample B, Sample C, etc.) were used, variations in contraction behavior were observed, irrespective of the presence or absence of surface active materials. After a systematic examination [19] of all likely sources of error, it was found that traces of bromine in the LiBr solution have a profound effect on the contraction.

TABLE I

pH of rinsing solution	4	Tap water	9
% l decrease*	47 ± 1	50 ± 1	49 ± 1
% r increase*	38 ± 6	41 ± 10	39 ± 5
% v increase	2.9 ± 2.0	4.7 ± 2.5	4.1 ± 3.3

* The 90% confidence limits are quoted.

Supercontraction in LiBr solution containing traces of bromine. To determine the influence of bromine (which, under these conditions, would exist largely as the tribromide (Br_3^-) ion), known amounts were added to 100% LiBr solutions prepared from the various samples available (*i.e.*, 100 g. LiBr in 100 ml. water). (For details see Appendix.)

Normal wool. As shown in Table II (*e.g.*, Solutions 1 and 2; Solutions 5, 6, and 7), the addition of small quantities of bromine to the LiBr solution reduces the contraction of clean and detergent treated fibers (1.92 meq. sodium lauryl sulfate/100 g. wool). With a bromine concentration about 10^{-4} M in LiBr,[4] the contraction was reversible on subsequent washing in boiling water. On re-using the same solution with fresh fibers each time, the concentration of bromine was found to decrease and the contraction correspondingly to increase. The effect of prolonged treatment of the solution with wool is shown in the Appendix, and it is indicated that this method of purifying the solution is undesirable [4]. The material extracted into the solution by this method completely eliminates irreversible contraction [20] and shows an absorption peak at about 275 mμ, but this is not due to bromine since it is not removed by sodium thiosulfate and only partly removed by norite. It would seem likely that the material is of a proteinaceous nature. The irreversible contraction does not seem to approach the maximum value previously found (50%), while the bromine concentration

[3] For the sake of brevity, "contraction" will be used henceforth instead of "supercontraction."

[4] In a prior note by the authors (*Chemistry and Industry* **47**, 1424 (1956)), the bromine concentrations are incorrectly stated.

TABLE II

Solution††	Optical density of peak at 273 mμ*	Optical density of peak at 303 mμ	Contraction, % Clean	Contraction, % Detergent treated
1. LiBr soln. prepared [9]	0.12	0.12	41	32
2. Soln. 1 + ca. 5×10^{-4} *M* Br_2 Soln. pale yellow	0.76	0.3	10	8 Soln. colorless after use
3. Soln. 2 re-used			26	10
4. Soln. 3 re-used			26	24
5. Sample B	0.43	0.52	50	51
6. Soln. 5 + ca. 10^{-4} *M* Br_2 Soln. pink			24	18 Soln. still pink
7. Soln. 6 + ca. 2×10^{-4} *M* Br_2			6	4
8. Sample C	0.7†	1.3	52	49
9. Soln. 8 + ca. 2×10^{-4} *M* Br_2 Soln. deep yellow			49	48 Soln. still yellow
10. Sample D	0.3	0.45	52	50
11. Soln. 10 + ca. 10^{-4} *M* Br_2			6	4
12. Sample E	0.75	1.4	50	48
13. Soln. 12 + ca. 10^{-4} *M* Br_2			13	5
14. Sample F	0.22‡	0.1	52	52
15. Soln. 14 + ca. 10^{-4} *M* Br_2			4	8
16. Soln. 15 + few crystals $Na_2S_2O_3$			49	48
17. Sample A_2	0.46	0.2	37	37
18. Soln. 17 + $Na_2S_2O_3$			52	
19. Soln. 17 + ca. 10^{-4} *M* Br_2			32	10
20. Re-prepared Soln. 19			12	8
21. Sample A_3	0.41§	0.26	30	18
22. Soln. 21 + $Na_2S_2O_3$			43	48
23. Soln. 21 used several times	0.48§	0.3	41	16
24. Soln. 21 + ca. 10^{-3} *M* Br_2				wool dissolves

* As shown in the Appendix, this peak is due to "free" bromine (or Br_3^-) although the actual optical densities quoted are complicated by the contribution from an impurity (possibly nitrate).

† High value here due to contribution of peak at 303 mμ to that at 273 mμ.

‡ After heating for 3 hr. at 100° C.: 0.28.

§ This increase is probably due to concentration of the solution.

†† Solutions of the various samples of LiBr are 100%, i.e., are made up by dissolving 100 g. LiBr in 100 ml. water; where a certain concentration of Br_2 is referred to, this has been made up by adding an appropriate volume of saturated Br_2 water. (Full details are given in the section "Materials and Methods".)

is much greater than about 10^{-5} *M*. For some brands of LiBr, the amount of bromine which can be added to the solution before contraction is eliminated is greater than for others. In such cases, the color changes produced on adding small amounts of bromine to the LiBr solution indicate that the bromine is probably reacting with some impurity, since these solutions were still colored even after all the bromine had been exhausted (*e.g.*, Solution 9 in Table II).

The addition of a few crystals of sodium thiosulfate to the LiBr solution completely removes all traces of bromine (see Appendix) and permits maximum contraction. Boiling or treatment with norite will not remove the bromine as effectively. Purification of the salt by reprecipitation with chloroform from a saturated acetone solution also removes traces of bromine. The addition of sodium thiosulfate is not necessary with all the brands of LiBr examined before maximum contraction is possible.

Differences between the various LiBr samples were observed in respect to physical appearance, surface active impurities as judged by their surface pressures, and contraction behavior. Addition of 10^{-4} *M* bromine to Sample A_2 (surface pressure, 3.6 dyne $cm.^{-1}$) gave a result similar to that with Sample A_1 (surface pressure, 15 dyne $cm.^{-1}$), namely a big difference in contraction behavior between fibers with and without adsorbed detergent. These results show that the amount of bromine present is extremely critical if this difference in behavior is to be shown; apparently in Sample A_1 the bromine concentration was just right.

As already mentioned, fibers treated in LiBr containing small amounts of bromine contract less than when bromine is absent. On subsequent treatment with "purified" LiBr solution, these fibers still show a contraction of about 50%. However, this increased contraction is not due to the extra time of heating. For example, a solution of LiBr (Sample A_3) was used for 5 different contraction experiments (each 3 hr. at 100° C.), and the contraction increased from 30 to 41%. On the other hand, fibers treated with LiBr solution (Sample A_3) for 15 hr. at 100° C. showed an increase to only 34%. Treatment for longer periods weakened the fibers mechanically.

Modified wool and other keratins. The contractions of modified wool and other keratins, using 100% LiBr (Sample A_1) solution which contained the critical bromine concentration, are shown in Table

III. Using the other LiBr samples, attempts to prepare a solution containing this critical bromine concentration were not always successful, possibly due to the volatility of bromine itself and to the presence of trace impurities, *e.g.*, metal ions, with which it is possible for bromine to combine.

These experiments were repeated using another solution of LiBr (Sample A_3) to give the figures shown in parentheses. In some cases, the contraction has decreased, probably due to the greater bromine concentration of this solution. (These results should be compared with those in Table V where bromine has been eliminated by the addition of sodium thiosulfate.) The contraction of Lincoln wool as shown here is similar to that found by Alexander [4], and it is significant that in all cases, except for crossbred wool, the contraction is dependent on the pH of the after-treatment.

Wools treated with surface active agents and dyes. As already mentioned, the LiBr was found to contain surface active materials. To determine their importance, known amounts of synthetic detergents were adsorbed on wool and the contraction determined using LiBr (Sample A_1) solution from which such materials had first been removed by treatment with norite. The bromine concentration of this solution, already found to be between 10^{-4}–10^{-5} *M*, was not altered by the charcoal treatment.

Fibers selected at random from a sample of wool on which 1.3 meq. sodium lauryl sulfate/100 g. had been adsorbed showed contractions of 4, 7, and 8% on subsequent rinsing in solutions pH 4, tap water, and pH 9, respectively. Thus the ability to contract was almost entirely removed by this pretreatment. Wool fibers pretreated with a cationic detergent C.T.A.B. showed similar contraction behavior. Accordingly the amount of detergent adsorbed was varied in an endeavor to determine the amount of detergent which could be adsorbed and still permit the wool to contract in LiBr solution. Such a study

TABLE III

Type of keratin	Contraction, % pH 4	Tap water	pH 9
Normal wool	47 (34)	50 (32)	49 (33)
Deaminated wool	40 (12)	41 (16)	24 (27)
Methylated wool	12 (12)	14 (16)	26 (29)
Horse hair	35 (7)	42 (8)	37 (21)
Human hair	22 (14)	27 (10)	33 (23)
Lincoln wool	17 (16)	— (16)	29 (28)

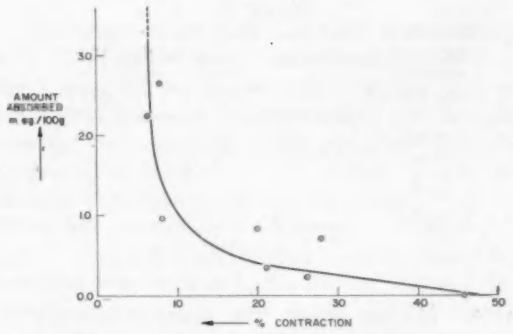
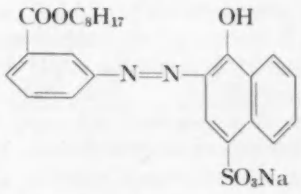


Fig. 1. Contraction of detergent treated fibers.

was of interest because, once having located the site of the adsorbed detergent, it might be possible to determine which portion (histological) of the fiber is of significance in the contraction process.

(*a*) *Effect of an anionic detergent and an anionic dye.* Varying amounts of sodium lauryl sulfate were adsorbed on wool from solutions whose concentrations ranged from 0.001–0.00004 *M*. At lower concentrations, determination of the amount of adsorption is difficult [19]; accordingly, a surface active dye was used. This dye has approximately the same surface area (calculated using Catalin molecular models)



as sodium lauryl sulfate when coiled to a maximum. Its adsorption from a 0.0001 *M* solution in 40% ethanol was determined spectrophotometrically.

As shown in Figure 1, this pretreatment greatly reduces the contraction when about 0.2 meq./100 g. is adsorbed, and almost entirely eliminates it with about 1.0 meq./100 g.

When similar amounts of sodium lauryl sulfate were adsorbed on isoelectric wool, the decreases in contraction were only slightly less than those for normal wool (pH about 6).

Attempts were made to remove the detergent to see if the ability to contract could be restored.

TABLE IV

Amount of detergent adsorbed (meq./100 g.)	Contraction, %	
	pH 4	pH 9
0.00	45	50
0.94	45	50
0.98	33 17	49 33
1.20	17	37
~2	3	1

Aicken [1] has shown that detergents cannot be desorbed even after boiling with water for long periods. No detergent could be removed by treatment with a cationic detergent in the presence of 0.01 *N* HCl, but when the wool (1.3 meq. sodium lauryl sulfate/100 g.) was extracted with absolute ethanol containing KCl (for ion replacement purposes—KCl being soluble in ethanol), the ability to contract was partially restored, contractions of 19, 24, and 34% subsequently being obtained for the various pH's of aftertreatment.

(*b*) *Effect of a cationic detergent.* C.T.A.B. was adsorbed on wool; the contractions obtained for the varying amounts adsorbed are shown in Table IV. From these results, it appears that pretreatment with a cationic detergent reduces the contraction and that the decrease is not as marked as with the anionic agent. Wool fibers dyed with gentian violet, which is similar in cationic nature to C.T.A.B., also showed a reduction in the amount of contraction obtainable, namely 17 and 38% on rinsing in pH 4 and pH 9 buffers, respectively.

(*c*) *Effect of a nonionic detergent.* Wool on which the nonionic detergent Triton X-100 (3.1 mmol./100 g. wool calculated assuming a molecular weight of 646) had been adsorbed contracted 39 and 46% after rinsing in pH 4 and pH 9 buffers, respectively. Hence the presence of this substance appears to have little influence on the contraction obtainable in LiBr solution, although the method of analysis is not fully adequate to determine accurately the amount of adsorption.

IV. Contraction in LiBr Solution Freed from Traces of Bromine

For all experiments described in this section, LiBr solution freed from traces of bromine by the addition of a few crystals of sodium thiosulfate was used. A control experiment using the same concentration of sodium thiosulfate in water did not produce any appreciable contraction.

(*a*) *Wool and other keratins.* Treatment of wool and other keratins with 100% LiBr solution for 3 hr. at 100° C., followed by rinsing in the boiling buffers indicated, produced the contractions shown in Table V.

If these results are compared with those in Table III, it will be seen that, in nearly all cases, any differences due to the pH of the aftertreatment are eliminated and that there is a marked increase in contraction for methylated wool. Further, pretreatment with detergents has no effect.

(*b*) *Effect of temperature.* Wool was treated with 100% LiBr for 3 hr.; the contractions obtained at the temperatures indicated are shown in Figure 2 (S_1 represents the contraction when the fiber is removed from the LiBr solution and S_2 that when the same fiber is rinsed in boiling water).

Above about 75° C., the contraction is irreversible under these conditions. At 70° C. it is reversible, but when allowed to proceed for 21 hr., it becomes irreversible and the maximum contraction is approached (43%). According to Alexander's results for Lincoln wool [4], contraction is reversible at 80° C., but Beauregard et al. [7] have obtained irreversible contraction at this temperature although their value is not as great as that found here. No significant contraction was obtained after long reaction periods (1 week) at about 20° C. even when a 75% LiBr solution was used [see (*c*)].

(*c*) *Effect of concentration.* The effect of concentration at 100° C. is shown in Figures 3 and 4. The *final* contraction after 3 hr. is approximately the same when solutions of 75–125% (6.6–10.6 *M*) LiBr are used. For a 50% (4.4 *M*) solution, only about 25% contraction is observed even after 12 hr. At 125% (10.6 *M*), the rate is much slower than for

TABLE V

Type of keratin	Contraction, %		
	pH 4	Tap water	pH 9
Normal wool	48	48	49
Deaminated wool	37	37	39
Methylated wool	47	47	48
Horse hair	25	26	26
Human hair	29	31	26
Lincoln wool	36	36	35
Detergent treated wool (1.92 meq. sodium lauryl sulfate/100 g.)	48	48	49

the other solutions with which it was possible to obtain 50% contraction.

For the concentrations above 50%, the contraction increases markedly over a fairly narrow interval of time, this being most prominent with the 125% solution. For times up to about 60 min., contraction is reversible, but after about 90 min., it rather suddenly becomes irreversible.

(*d*) *Visual observations.* Some visual observations on the contraction behavior of the fibers should be pointed out. At the beginning when contraction is reversible, the fibers are not very tightly coiled in the LiBr solution and immediately unravel into haphazard waves on rinsing in water. As contraction begins, the fibers are tightly coiled in the solution and, on rinsing in water, assume a very tightly crimped appearance. When contraction has approached a maximum, the fibers are still tightly coiled, but in general, straighten out somewhat in boiling water and seem too bulky to be able to crimp quite so much. When the contracted fibers are removed from the LiBr solution, they are rubbery, slightly opaque in appearance, and readily extensible. On rinsing in water, they contract further [4], become brittle, and cannot be extended very far without damage. On heating the brittle contracted fiber for a short time in LiBr solution, the original contracted length and rubberlike nature is restored. The disappearance of rubberlike elasticity is similar to that observed by Elöd and Zahn [14] for horse hair contracted in 40% resorcinol, and, according to them, keratin fibers are only rubbery under the experimental conditions of supercontraction.

(*e*) *Effect of salts other than LiBr.* LiCl (12 *M*) and LiI (9 *M*) solutions showed contractions similar to those for the bromide (about 50%). In both cases the addition of (approximately) 10^{-3} *M* chlorine and iodine respectively still permitted significant contractions, namely 10 and 25%. Hence the amount of halogen which may be present before irreversible contraction is eliminated is very much greater than for LiBr solution. With comparable amounts of bromine in LiBr solution, the wool dissolves.

Using solutions of lithium salts other than the halides, namely sulfate, oxalate, and nitrate at pH approximately 6, saturated at room temperature, no contraction was obtained. However, this does not constitute a comparison on the same molar basis as that for the bromide. Lithium nitrate was the only one of these solutions with which such a com-

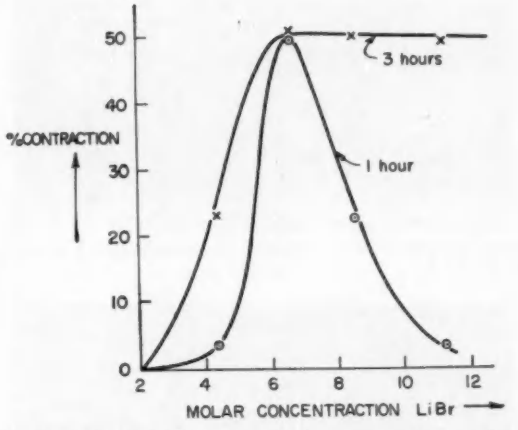


Fig. 3. Effect of LiBr concentration on contraction after 1 and 3 hr.

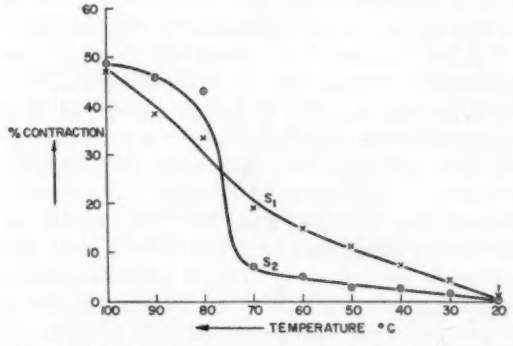


Fig. 2. Contraction after treatment with 100% LiBr solution for 3 hr. at various temperatures. (S_1, contraction on removal from LiBr solution; S_2, contraction after subsequent rinsing in boiling water.)

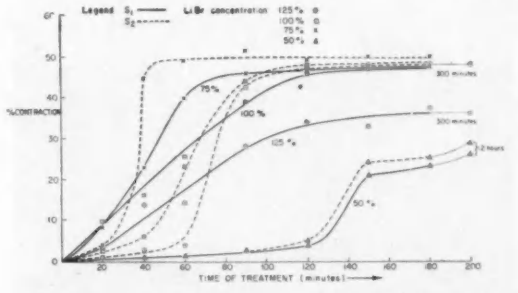


Fig. 4. Rate of contraction for various LiBr concentrations. (Temperature 100° C.) (S_1, contraction on removal from LiBr solution; S_2, contraction after subsequent rinsing in boiling water.)

parison could be made, due to its high solubility at an elevated temperature. After 3 hr. at 100° C., a 9 *M* $LiNO_3$ solution gave 41% contraction, showing that wool fibers will contract in lithium salt solutions, other than halides, if the salt is sufficiently water soluble.

On treating wool fibers with a 7 *M* NaBr solution containing 10^{-3} *M* bromine, the fibers were weakened but did not dissolve (cf. Table II, Solution 24). Hence it would appear that, although the tribromide ion attacks the fibers, the process of solution is accelerated by the presence of lithium ions.

(*f*) *Microscopical examination of contracted fibers.* Microscopical examination of fibers subjected to treatment with lithium halides containing trace amounts of added halogen showed varying amounts of fiber modification. Fibers were treated for 3 hr. at 100° C. with the following systems:

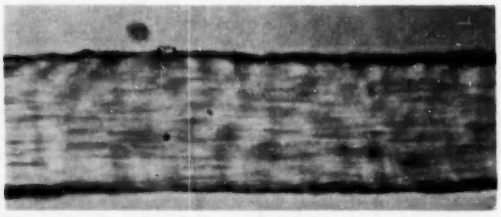


Fig. 5. Fiber after treatment with 8.7 *M* (100%) LiBr containing about 10^{-4} *M* bromine for 3 hr. at 100° C. Contraction 4%.

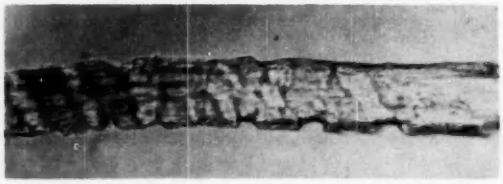


Fig. 6. Fiber after treatment with 9 *M* LiCl containing about 10^{-3} *M* chlorine for 3 hr. at 100° C. Contraction 10%.

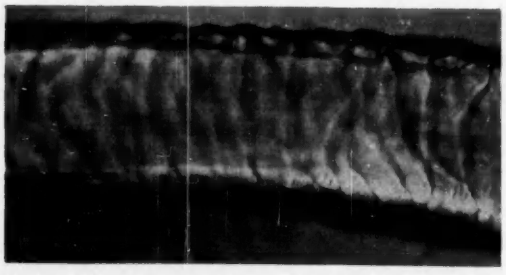


Fig. 7. Fiber after treatment with 12 *M* LiI containing about 10^{-3} *M* iodine for 3 hr. at 100° C. Contraction 25%.

Solution A: 8.7 *M* (100%) LiBr + ca. 10^{-4} *M* bromine
Solution B: 12 *M* LiCl + ca. 10^{-3} *M* chlorine
Solution C: 9 *M* LiI + ca. 10^{-3} *M* iodine

followed by washing in boiling water.

Using Solution A which contains sufficient bromine to permit either reversible or no permanent contraction, the scales appear rounded or partially removed (Figure 5). This might imply that partial modification of the scale structure permits reversible contraction. However, fibers treated with (i) ethanolic KOH [23]; (ii) 10^{-4} *M* bromine solution at 100° C. for 3 hr.; (iii) 7 *M* NaBr containing 10^{-4} *M* bromine under the conditions as in (ii), all of which can be shown to modify or partially remove the scales, still show irreversible contraction when subsequently treated with LiBr solution. This behavior is quite distinct from that when bromine is added directly to the contracting medium. Although the scales seem to be almost entirely removed by the treatment outlined in (iii), nevertheless the fibers on subsequent treatment with LiBr solution still show a folded structure typical of normal contraction, although the surface appears modified.

After treatment with Solution B, the fibers showed a greater surface modification than that described above, whole sections of cuticular material being removed at comparatively regular intervals from all around the fiber periphery (Figure 6). As already shown, the presence of chlorine in LiCl solution did not produce an effect on contraction as marked as that shown by Solution A. In the case of treatment with Solution C (Figure 7) the fibers also showed surface modification of a kind different from either of those described above, but here also the effect on contraction was not as marked as for Solution A.

Figure 8 shows a fiber reversibly contracted in "purified" LiBr solution (75%) for 40 min. and indicates that one side of the fiber contracts in a manner different from the other. For a fiber showing 50% contraction, both sides have contracted, but the pattern of folding is not the same and two levels of focus are required (Figure 9). If the reaction is allowed to proceed for a long time with a solution not sufficiently concentrated (50%) to permit maximum contraction within a reasonable time, there seems to be a considerable amount of internal modification and unsymmetrical contraction of the type envisaged by Mercer [25] (Figure 10). Such differences in contractibility have been observed in many fibers,

and recently it has been possible to follow the course of this folding during the reaction with the aid of a hot stage microscope [22].

V. Discussion

The present study makes it possible to advance our understanding of the ability of LiBr to promote supercontraction by elucidating the main source of variability in earlier work. Thus reproducible quantitative studies of such important variables as type of keratin, concentration of the LiBr solution, temperature, and duration of treatment, can now be made. The purity of the LiBr salt has been shown to be important, the major contaminant being bromine, present in minute concentration (10^{-4}–10^{-5} M), but nevertheless exerting a marked influence upon supercontraction, particularly if the wool has previously been treated with surface active agents. In the view of this it is desirable to consider separately the behavior of the "bromine-free" and "bromine-containing" solutions. Before discussing the LiBr system in detail, it may be pointed out that wool will contract in solutions of lithium salts other than the bromide provided they are sufficiently soluble in water. For the conditions used here, the anion appears to have little influence, although solubility difficulties have limited the comparison to the chloride, bromide, iodide, and nitrate. This differs from the findings of Crewther and Dowling [11], although their experimental conditions are also different.

(a) *LiBr solutions freed from bromine.* With the bromine-free LiBr solutions, the following points have been established:

(i) Crossbred wool will contract up to 50% of its original length, the contraction being independent of the pH of the aftertreatment between 4 and 9.

(ii) Differences in amount of contraction exist between various types of keratin (*e.g.*, type of wool, modified wool, hair), but neither the pH of the aftertreatment nor the adsorption of surface active agents or dyes have any effect.

(iii) Contraction may be reversible or irreversible (on washing out the LiBr) depending on the temperature and time of treatment.

(iv) Contraction is independent of modification to the fiber surface, suggesting that this is unimportant in the phenomenon.

The ability of concentrated solutions of LiBr to bring about contraction has been ascribed by Alexander [4] to hydrogen bond rupture and is thus similar to the mode of action postulated by Elöd and Zahn [14] in the case of phenols, urea, and formamide. These authors assume that the driving force which shortens the chains (and hence the fiber) arises mainly from entropy effects; that is, the fiber exhibits rubberlike elasticity once the hydrogen bonds have been broken. Elöd and Zahn [14], in particular, have illustrated the close correlation between supercontraction and entropy effects in keratin fibers. The physical behavior of the fibers in the present investigation is quite consistent with this suggestion.

Contraction with LiBr has been shown to be reversible or irreversible depending upon the temperature and duration of treatment. As shown in Figures 2 and 4, contraction is at first reversible and

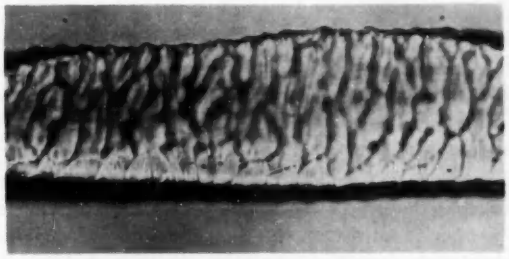


Fig. 8. Fiber treated with 75% LiBr at 100° C. for 40 min. Contraction about 30%.

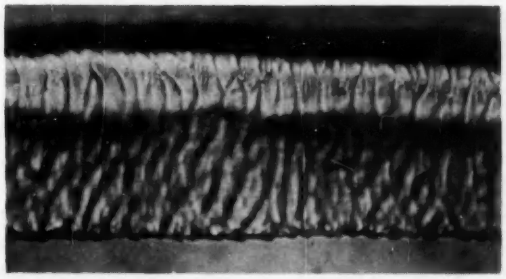


Fig. 9. Fiber after treatment with 75% LiBr at 100° C. for 120 min. Contraction 50%.

Fig. 10. Fiber treated with 50% LiBr at 100° C. for 12 hr. Contraction 25%.

then suddenly becomes irreversible as though a barrier to irreversible contraction has been overcome. Below the temperature found to be critical for the conditions used, the reaction slows down considerably, *e.g.*, a contraction after 3 hr. at 70° C. resembles that after 40 min. at 100° C. at the same concentration.

The reversibility or otherwise of contraction suggests that two types or, what may amount to the same thing, two main regions of hydrogen bonding, are involved. The two main types may be related to different strengths of hydrogen bonding (or interacting dipoles [10]). If it is a reflection of inter- and intra-molecular hydrogen bonding, then changes in the infrared dichroism during the process of contraction should be significant. The two main regions might either be the amorphous and crystalline regions, or, more likely, the ortho- and para-cortex. However they are described, it seems not unlikely that the strength of hydrogen bonding and the ease of accessibility will differ in the two cases. Thus it is tempting to assume that the reaction of LiBr is first to break the weaker (or more accessible) hydrogen bonds, the reaction at this stage being reversible; subsequently the stronger (or less accessible) hydrogen bonds are broken and this allows the fiber to adjust its shape freely under the driving (entropy) forces, tending to produce a less organized structure.

According to Mercer [25], conditions of treatment milder than those required to produce uniform contraction of the whole fiber produce unsymmetrical contraction of one side (*o*-cortex) and he adduces that this is evidence for the lower stability of this section of the fiber. Unsymmetrical contraction might therefore explain the coiled appearance of the fibers as they contract, and also the change in direction of coiling which is sometimes observed. However, apart from considerations of stability, there is also the possibility of different rates of penetration of the contracting medium in the two segments. Haly [21] has shown that the *p*-cortex is always on the outside of a contracted fiber. This might indicate that the *o*-cortex contracts more readily or more rapidly than the *p*-cortex, and might account for the smaller contraction of hair, which apparently contains a greater amount of para-like material than does wool [13]. Further, the *o*-cortex is comparatively richer in glutamic and aspartic acids [18] and therefore might be expected to be more negatively charged and consequently modified more by methylation than the *p*-cortex. This might account for the large decreases in contraction of wool after methylation [8] when the ortho- or more easily contractile segment has been modified to a greater extent.

Once irreversible contraction has been established, contraction increases on washing out LiBr (for example, see Figure 2). This is most noticeable when fibers are irreversibly contracted in 125% LiBr solution, and might be a reflection of the large number of LiBr molecules absorbed in the fiber from solutions of these concentrations, that is, a kind of "salting in" effect similar to that shown by the increase in solubility of several amino acids, *e.g.*, cystine, in LiBr solution.

For the concentrations above 75% (6.6 *M* LiBr) studied, the rate of contraction becomes slower as the concentration increases. Possibly these higher concentrations lead to a rapid surface dehydration so that the fiber is, in a sense, "case-hardened" and thus the solution takes a longer time to penetrate. In this connection it is relevant to point out the considerable increase in surface tension and decrease in vapor pressure for the solutions examined. (Surface tensions: 88.9, 80.6, 78.6, and 76.1 dyne $cm.^{-1}$, and vapor pressures: 1.5, 4.5, 8.0, and 11.0 mm. at 20° C., for 125, 100, 75, and 50% LiBr, respectively.) No satisfactory explanation can be offered as yet for the behavior shown by the 50% solution, namely irreversible contraction at all stages.

(b) *LiBr solutions containing bromine.* In these systems the salient points seem to be:

(i) The presence of traces of bromine reduces the contraction of both clean and detergent treated fibers, a concentration of about 10^{-4} *M* generally eliminating the contraction altogether.

(ii) With bromine concentrations in the range 10^{-4}–10^{-5} *M* (as is present "naturally" in some LiBr samples), differences in contraction between the various types of keratin and also between clean and detergent treated fibers are found; in some cases, the latter show little contraction under conditions where the former give the maximum value (ca. 50%). The contraction is also dependent on the pH of the aftertreatment between pH 4 and 9. With the detergent treated fibers, the ionic nature of the detergent appears to be of importance, the cationic being less effective than the anionic, while the non-ionic is apparently ineffective.

(iii) A clean or detergent treated fiber which

shows no contraction under the above conditions shows its normal contraction behavior after a subsequent treatment with a LiBr solution free from bromine.

(iv) With a bromine concentration about 10^{-3} *M*, the wool dissolves almost completely under conditions where the bromine alone only weakens the fiber and the LiBr alone only causes supercontraction.

The most obvious explanation of the effect of these traces of bromine, or more correctly tribromide ions (Br_3^-), is that they react with the fiber, most probably with the cystine residues, although certain other residues may also be involved [33]. Rupture of the disulfides would provide a ready explanation for the dissolution of the fiber in the stronger bromine solutions (10^{-3} *M*) and is consistent with the known reactivity of bromine in concentrated solutions of bromides [2].

For the lower concentrations (about 10^{-4} *M*) the total amount of bromine available is approximately sufficient to oxidize all the cystine present, assuming oxidation to proceed only to cysteic acid. However, as shown in Table II (Solutions 2–4), not all the bromine is removed by successive treatments with wool under the conditions used here, but this may well be due to the slow rate of diffusion up to and into the fiber at these low bromine concentrations.

These considerations suggest that only the outermost regions of the fiber are affected and thus that some surface or "skin" effect is involved. If this is so, the marked influence of surface active agents is not unexpected since these are likely to be concentrated at the surface of the fiber. The markedly greater effect of the anionic type suggests that the basic side chains are of particular importance.

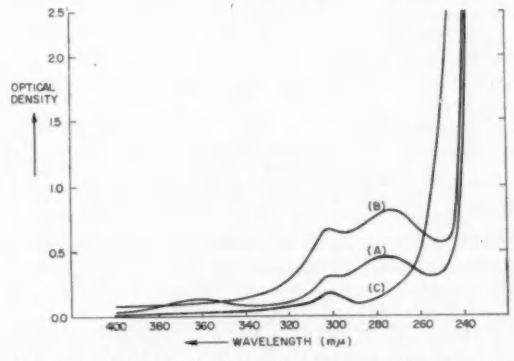


Fig. 11. Ultraviolet absorption spectra of (*a*) 100% LiBr solution. (*b*) Solution (a) after addition of 10^{-4} *M* Br_2 and used once for supercontraction. (*c*) Solution (a) after addition of $Na_2S_2O_3$.

The reaction of wool with the trihalide ions is not the same in all cases. It has been shown [2] that the apparent relative reactivity for these active intermediaries is $I_3^- < Br_3^- < Cl_3^-$; here, however, the tribromide ion seems the most active. Apart from considerations of stability, there is no information concerning the rate of penetration or the rate or specificity of reaction of these ions with wool. It is improbable that the effect is due to physical blocking by the Br_3^- ion because the effect is less noticeable with the larger I_3^- ion. On the other hand, if it is due to some chemical grouping, then any interpretation must also be able to explain the apparent subsequent normal contraction behavior shown [point (iii) above].

VI. Acknowledgments

The authors wish to thank Dr. A. R. Gilby for carrying out surface pressure measurements and Mr. A. R. Haly for assistance with photomicrography.

Appendix

Traces of bromine in LiBr solutions

A solution of LiBr prepared from constant boiling redistilled HBr and recrystallized Li_2CO_3 examined spectroscopically in the range 240–400 mμ showed an inflexion at about 273 mμ and a peak at 303 mμ. The peak at 273 mμ is probably due to the tribromide ion (Br_3^-), for when a small amount of bromine was directly added to the solution, this peak increased, and after addition of thiosulfate virtually disappeared (see Figure 11). Neither peak was affected by treatment of the solution with norite. The peak at 303 mμ was not due to any surface active component, for it was still present in solutions of negligible surface pressure. As the peak at 303 mμ was evident in the spectrum of a solution of NaBr and not in that for LiCl, it would appear that it is derived from the HBr used to prepare bromide salts. However, a solution of $LiNO_3$ showed a very strong absorption at 303 mμ due to the nitrate ion, thus suggesting that trace amounts of nitrates may be responsible.

In the light of these observations, 100% solutions of LiBr from different manufacturers were examined

spectroscopically, and in all cases peaks at 273 and 303 mμ were detected. A few spectra typical of these LiBr solutions are shown in Figure 12. The spectroscopic details for about 50 such solutions under varying conditions of bromine, and the corresponding contractions, are reported elsewhere [19].

The small amounts of bromine present in solutions of LiBr could arise from aerial oxidation, as shown by the calculation [19] of $\Delta G°$ for the equilibrium:

$$2Br^- + \tfrac{1}{2}O_2 + 2H^+ \rightleftharpoons Br_2 + H_2O$$

Above a certain concentration, about 10^{-3} *M*, small amounts of bromine in the LiBr solution have a drastic effect on wool, sufficient to dissolve it almost completely. Bromine water alone at this concentration and under these conditions weakens the fibers but does not dissolve them, whereas for corresponding treatment with LiBr solution alone, only contraction is induced.

LiBr solution, after treatment with wool (Solution A), using conditions more drastic than those employed for contraction (1 g. wool/30 ml. LiBr solution heated for 3 days at 100° C.) has been examined spectroscopically. Under these conditions there is no significant loss in weight, whereas when sufficient bromine was added to this solution to make it about 10^{-3} *M* with respect to bromine, 90% of the wool dissolved (Solution B). For this bromine concentration (Solution C) in water alone and under these conditions, 60% of the wool was recovered. Thus the difference in reactivity of Solutions A, B, and C becomes very apparent. The ultraviolet spectra of these solutions is shown in Figure 13.

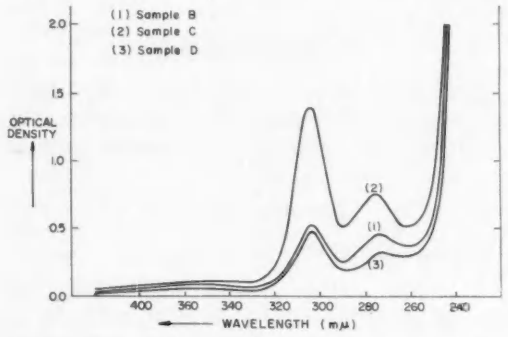


Fig. 12. Ultraviolet absorption spectra of 100% solutions of various samples of LiBr. (1) Sample B, (2) Sample C, (3) Sample D.

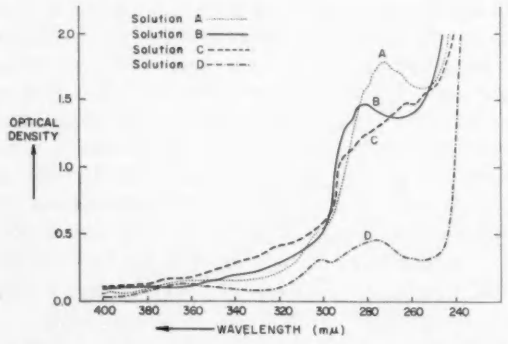


Fig. 13. Ultraviolet absorption spectra of various solutions after contact with wool for 3 days at 100° C. (1) Solution A, 100% LiBr. (2) Solution B, 100% LiBr containing 10^{-3} *M* Br_2. (3) Solution C, 10^{-3} *M* Br_2 in water. (4) Solution D, 100% LiBr solution before use.

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The Methylation of Cellulose Xanthate[1]

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Abstract

The distribution of xanthate groups along cellulose chains in commercial viscose solutions very probably affects the processing qualities of the viscose and also the physical properties of the spun yarn. The rayon manufacturer, therefore, as well as the cellulose chemist, is interested in knowing what that distribution is. Xanthate groups are too unstable to permit direct determination of their location; attempts have been made to fix their location by quantitative replacement with methoxyl groups. After hydrolysis of the methylcellulose thus produced to methylglucoses, various means have been used to identify the latter, but the results have not been sufficiently accurate to determine the positions of the original xanthate groups. In the present work use was made of chromatographic methods to separate and identify the products of hydrolysis. However, during a careful re-examination of the methylation procedure it has been found that about 20% of the xanthate groups are not replaced but are converted to the S-methyl ester. In this form they are lost during hydrolysis. Hence, although adequate means are now available for determining the positions of methyl groups in methylcellulose, better means of replacing xanthate groups must now be sought if the original problem is to be solved.

Introduction

Because of the great industrial importance of the viscose process, the reaction between alkali cellulose and carbon disulfide has been studied extensively. The product of this reaction, cellulose xanthate, may be regarded as an ester of sulfothiocarbonic acid, HO—CS_2—SH, and the polyhydric alcohol cellulose; actually, the sodium salt of this ester is obtained in the commercial process, the acid being dibasic. The reaction may be written

$$\text{Cell—OH} + \text{NaOH} + CS_2 \rightarrow \text{Cell—O—}CS_2\text{Na} + H_2O$$

where only one hydroxyl on the cellulose chain is indicated.

Theoretically it is possible to introduce three xanthate groups into every glucose residue of the cellulose chain. Complete substitution, however, is rarely if ever achieved. In the viscose process a much lower degree of substitution is sufficient to make a product soluble in dilute lye solution; a xanthate ratio of 0.6–0.7 in freshly prepared viscose is common, and this is further reduced to 0.3–0.5

[1] Presented before the Division of Cellulose Chemistry, American Chemical Society, at the 131st Meeting, Miami, Florida, April 7–12, 1957.

during ripening prior to spinning. (Xanthate ratio is defined as the average number of xanthate groups per anhydroglucose unit; hence the highest ratio theoretically possible is 3.)

Since there is only about one xanthate group for every two glucose residues in the cellulose molecule for commercial viscoses, the distribution of these groups along the chain can vary greatly. In view of the heterogeneous character of the cellulose fibers and fibrils, with individual chains extending through several crystalline and amorphous regions differing markedly in their accessibility to chemical reaction, some segments of the chains may be highly xanthated while others remain almost untouched. These irregularities in xanthation may significantly affect important processing characteristics of the viscose; *e.g.,* filterability, while the distribution of these groups during regeneration may also have a profound effect upon the physical properties of the rayon fibers. It is widely thought that one of the helpful effects of ageing or ripening viscose solutions is a redistribution of xanthate groups, resulting in greater uniformity. Knowledge about these matters should therefore be of value in finding ways to improve the processing and to obtain a better product.

Even if we consider only one anhydroglucose link in the cellulose chain, there is still ample room for variation. With three available reaction sites, on carbons 2, 3, and 6, three mono- and three dixanthates are possible in addition to the trixanthate (for a xanthate ratio less than 0.5 the majority of chain links will of course not be substituted at all). To the chemist, and probably ultimately to the manufacturer of rayon, it is of considerable interest to know whether all three of these sites are about equally reactive or one is markedly more or less reactive than the other two.

Because of the great practical as well as scientific interest in the problem of distribution of xanthate groups in viscose, several attempts have been made to find means to determine it. None has yet been reported that is even approximately satisfactory. Besides the inherent complexity that exists at any moment along the xanthated cellulose chain, the difficulties of determination are compounded by the instability of the xanthate group attached to the molecule. Except at temperatures near or below 0° C., viscose solutions spontaneously decompose with loss of xanthate groups, and small changes in the concentration of the buffering salts always present in commercial viscose or additions of even mild reagents accelerate the decomposition.

The first objective, therefore, in any study of xanthate distribution is to tag in some way the positions of the xanthate groups until these can be identified. Although attempts have been made to strengthen the attachment of the xanthate groups to the chain through substitution, the way most frequently used to tag the sites has been to replace each xanthate by a methyl group firmly bound to the anhydroglucose unit by an ether bond. This method was introduced by Lieser [7] and has been used since by several investigators [2, 5]. Once the position of the substituting groups has been fixed, their identity and number must be determined: what proportions of the glucose residues carried zero, one, two, and three xanthate groups and, in the case of one and two, to which carbon atoms were they attached? To solve these problems, use has been made of differences in reactivities of the remaining hydroxyl groups. For example, sodium paraperiodate under proper conditions reacts exclusively with glycol groups and can therefore be used to determine the number of unreacted hydroxyls in the 2 and 3 positions. Tosylation followed by iodination has been used to determine the number of remaining primary hydroxyls (in the 6 position). Altogether, a rather elaborate system of reactions is required to account for all possible combinations of unreacted hydroxyls; the positions of the xanthate groups must then be determined by difference with, in some cases, considerable uncertainty due to combination of experimental errors. In a more direct approach, the methylated cellulose is hydrolyzed down to the component substituted glucoses, which are then identified. With the advent of chromatographic procedures, the last step has become experimentally rather simple and accurate.

After a study of the available literature, the following procedure appeared to offer most promise for

TABLE I

Xanthate ratio	Methoxyl content, %		
	Calc.	Found	Ratio
0.410	7.58	7.8	1.02
0.428	7.90	7.6	0.96
0.430	7.94	7.6	0.96
0.489	9.05	9.4	1.04
		Average	1.00 ± 0.04

success in determining the distribution of xanthate groups:

1. Replace all xanthate groups quantitatively by methyl groups.
2. Hydrolyze methylated cellulose down to glucose and methylglucoses.
3. Separate methylglucoses chromatographically.
4. Determine the amount of each type of methylglucose by suitable analytical methods.
5. Reconstruct the picture of the original cellulose xanthate.

This paper is concerned primarily with the first three of these steps, although the next two have also received attention to varying degrees. Only the last step will not be dealt with here, because difficulties encountered in the earlier steps made interpretation impractical.

Results and Discussion

When sodium cellulose xanthate is methylated, some free hydroxyls as well as the xanthate groups are involved; in fact, alkali cellulose, without addition of CS_2, is methylated with diazomethane or nitrosomethylurethane [2]. In order to avoid reaction with hydroxyls, therefore, and to confine the reaction to the xanthate groups only, the cellulose xanthate is precipitated and washed free from alkali and various salts. At the same time there should not be any appreciable loss of xanthate groups, which become less stable at low pH. Pure alkali-free cellulose xanthic acid (also termed neutral cellulose xanthate) was obtained by pouring the viscose as a thin stream into cold methanolic acetic acid; this gives a fibrous mass which is easily purified and handled in later steps. Analysis of samples prepared showed that less than 2% of the xanthate groups were lost during this procedure.

For the methylation itself two agents were tried. The first was a solution (0.4 *M*) of diazomethane in ethyl ether. At 0° C. methylation was slow. After 16 hr. less than 50% of the xanthate groups had been replaced; extrapolation of the data indicated that several hundred hours would be required for complete replacement, during which time appreciable reaction with free hydroxyls would also occur. Reaction at higher temperature to reach a practical rate was ruled out because of the instability of diazomethane.

Chen, Montonna, and Grove, following Lieser, found nitrosomethylurethane (which yields diazomethane) to be a suitable methylating agent, and we confirmed their experience. Analysis of the products of several such methylations showed approximately one methoxyl group present for every xanthate group originally present; Table I illustrates this point.

As a check to see that no methylation of hydroxyl groups occurred, viscose samples were precipitated in a 1% solution of HCl in methanol; this treatment split off all xanthate groups but gave a highly swollen product similar to that precipitated in acetic acid, in which the hydroxyl groups should be as readily accessible as in the cellulose xanthic acid. Treatment of this material with nitrosomethylurethane in methanol resulted in no appreciable methylation. These results together indicated that nitrosomethylurethane does replace xanthate groups in cellulose xanthic acid without addition to free hydroxyls. There was, however, one disturbing factor: in all the methylated samples a small amount of residual sulfur was found. (Analysis of methylated samples for sulfur is not reported in other published papers.) In view of the close agreement between the initial number of xanthate groups and final number of methoxyl groups, it was at first thought that this residual sulfur probably represented byproducts that had not been removed completely by washing, even when alkaline sulfide solutions were used.

These results seemed to justify going on to the next steps. Accordingly, samples of the methylcelluloses were hydrolyzed with sulfuric acid; the neutralized solutions were evaporated to dryness at reduced pressure and the residues dissolved with aqueous alcohol. The solutions were chromatographed with aqueous butanol-ethanol on Whatman No. 1 paper and the location of each sugar determined by spraying with aniline hydrogen phthalate. The amounts of glucose and methylglucoses were determined by the procedure of Rebenfeld and Pacsu [10].

The chromatographic method just outlined separates mono-, di-, and trimethylglucoses from one another and from glucose. There are known techniques for further separation of the various mono- and dimethylglucoses from one another [6], but our work never reached the stage where this was needed. The reason was that we could not recover from the hydrolyzates as many methoxyl groups as were in the methylcellulose before hydrolysis. The

discrepancy was finally linked to the residual sulfur in the methylcellulose already mentioned.

The accumulated evidence seemed to show that not all xanthate groups were replaced under the conditions of methylation used. On the other hand, the 1/1 correspondence between xanthate groups and methoxyl groups strongly suggested that all the former are involved in some way. These two conclusions can be reconciled if esterification instead of replacement takes place on some of the xanthate groups.

$$\text{Cell—O—}CS_2H + CH_2N_2 \rightarrow \text{Cell—O—}CH_3 + CS_2 + N_2 \text{ (replacement)}$$

and

$$\text{Cell—O—}CS_2H + CH_2N_2 \rightarrow \text{Cell—O—}CS_2\text{—}CH_3 + N_2 \text{ (esterification)}$$

In both reactions one methoxyl will be found in the product for each xanthate group originally present. It has been suggested [12, 15] that the S-methyl xanthate ester is unusually stable and the methyl group is not split off, quantitatively at least, in the conventional determination of methoxyl. We have not found this to be the case, although we have used essentially the same analytical procedure. Because of the higher molecular weight of the ester compared to the methyl derivative (252 and 176 resp.), accurate analysis should distinguish between the two; when only a small proportion of the ester is present, however, the analytical errors will hide such an effect. The presence of sulfur that cannot be removed by thorough washing supports the postulate that some ester has been formed.

Further evidence is provided by the action of acid upon the methylated cellulose xanthate. When a sample containing residual sulfur is heated at 100° C. for 3 hr. with 1 *N* HCl under reflux, there is loss of methoxyl, although a sample of commercial methylcellulose similarly treated showed no loss; some of the methyl groups in the first sample are thus differently attached. These qualitative observations are strengthened by the following quantitative examples. A sample of viscose with a xanthate ratio 0.49 was converted to cellulose xanthic acid and methylated. The product contained 2.9% sulfur. After hydrolysis to remove ester-bound methyl groups, the methoxyl content was found to correspond to 7.2% in the methylated xanthic acid. This agrees well with the value of 7.4% calculated by Equation 7. In another case, 83.6 mg. of methylated cellulose xanthic acid, containing 11.0% methoxyl and 6.4% sulfur, was hydrolyzed and the hydrolyzate separated chromatographically; 38.3 and 1.1 mg. of mono- and dimethylglucose were obtained. The following balance may be struck:

Methoxyls from S-methyl ester

$$.031 \times 83.6 = 2.60 \text{ mg.}$$

($M_S = 3.1\%$ from Equation 5)

Methoxyls from monomethylglucose

$$\frac{31}{194} \times 38.3 = 6.10$$

Methoxyls from dimethylglucose

$$\frac{62}{208} \times 1.1 = 0.33$$

Total 9.03

Methoxyls in cellulose xanthic acid

$$0.11 \times 83.6 = 9.20$$

Recovery = 98%

A separate portion of this same methylated xanthic acid was analyzed for methoxyl after hydrolysis to remove S-methyl ester; 8.0% was found. This compares very well with the 7.9% obtained by subtracting 3.1% calculated by Equation 5 for the ester-bound groups from the total of 11.0%.

Repeated experiments similar to those just described have led us to conclude that when cellulose xanthic acid is methylated under the conditions herein described, about 80% of the xanthate groups is replaced by methoxyls, while the remaining 20% forms S-methyl xanthate esters. The latter groups split off when the sample is hydrolyzed preparatory to chromatographic analysis, with resulting loss of methyl groups. From this it follows that only about 80% of the xanthate groups originally present can be determined in the subsequent steps. If one can assume that esterification instead of replacement takes place with equal probability on all xanthate groups in the cellulose xanthic acid, regardless of their being attached to the second, third, or sixth carbon atom, then the distribution of methoxyls representing the 80% xanthates replaced will also be the distribution of all xanthates, and esterification will not interfere except as it reduces the yield of methylglucoses. In view of the demonstrated differences in rate of substitution on the several types of hydroxyl groups in cellulose [14], such an assump-

tion of random esterification seems of highly doubtful validity. Until this point can be cleared up or until means have been found to effect methylation entirely by replacement of xanthate groups, without any ester formation, the procedure outlined at the beginning of this paper will not yield reliable information regarding the distribution of xanthate groups attached to cellulose in viscose.

Experimental Procedures

Cellulose Xanthic Acid

Pour about 12 g. of viscose as a thin stream into 300 ml. of ice cold 5% solution of acetic acid in methanol with constant stirring. Decant and wash the fibrous mass twice with 200 ml. of cold methanol.

Determination of Xanthate Ratio in Cellulose Xanthic Acid

Because of the instability of the xanthic acid, analysis for xanthate groups was not carried out directly on a weighed, dried sample. Instead, one sample of the viscose under study was analyzed for xanthate by the method outlined below. From a second sample the cellulose xanthic acid was precipitated and purified by the method just described and the product, without drying, was immediately analyzed by the same procedure. By comparing the results obtained with and without preliminary precipitation it was found that no appreciable loss (less than 2%) of xanthate groups occurred during preparation and purification of the cellulose xanthic acid. Thereafter the xanthate ratio of the acid was taken to be the same as the xanthate ratio of the corresponding viscose.

The procedure used was an unpublished modification of the method described by Samuelson and Gärtner [11]. Diluted viscose is passed through an ion exchange column containing the resin Amberlite IRA-400, which retains all byproduct sulfur ions and permits the cellulose xanthate ions to pass. The effluent from the column passes into a standard solution of cupric acetate. The cupric ions react quantitatively with the xanthate groups, and excess copper in the solution is determined by titration with standard versenate solution. Repeated checks of this procedure against other methods have shown it to be at least as accurate and precise, and considerably more rapid and convenient.

Methoxyl Determination

Methoxyls were determined by the Zeisel procedure modified by the omission of phenol [1]. Hydriodic acid was refluxed for 10–15 min. before introduction of initial charges of methylcellulose as recommended by Steele and Pacsu [13]. The reported methoxyl values are averages of two or more determinations and are reliable to about $\pm 0.2\%$.

Sulfur Determination

The Carius method was used [3]. The organic material was oxidized in a sealed tube with fuming nitric acid. The resultant sulfuric acid was precipitated with barium chloride and weighed as barium sulfate.

Methylation with Nitrosomethylurethane

The reagent was prepared by nitrosation of ethyl-N-methylcarbonate [4a] which in turn was made from ethyl chlorocarbonate [4b]. Twenty milliliters of the product was dissolved in 20 ml. of absolute methanol and the solution was added slowly (15 min.) to a sample of cellulose xanthic acid (about 1 g.) suspended in 50 ml. of absolute methanol kept at 2° C. After 3–5 hr. the methylcellulose was collected on a sintered glass filter and washed with methanol, then with water.

Hydrolysis of Methylcellulose

The method of Monier-Williams [8] was used with slight modification. A 100-mg. sample was dissolved in 3 g. of 72% sulfuric acid and allowed to stand overnight. The solution was then diluted to 300 ml. with water, and hydrolysis was completed by heating under reflux for 15 hr. on a water bath at 100° C. The solution was then made neutral to litmus with barium carbonate, filtered, and evaporated to dryness under reduced pressure at a temperature not exceeding 55° C. During the concentration a drop of 1 *N* hydrochloric acid was added occasionally to keep the solution slightly acid. The residue was extracted with aqueous alcohol for chromatographic analysis.

Chromatographic Analysis of the Hydrolyzed Methylcelluloses

For the chromatograms, Whatman No. 1 paper, in strips 19 in. long, was used. The developing re-

agent was the butanol-rich layer prepared by shaking together 5 parts water, 4 parts *n*-butanol, and 1 part ethanol [9]. When the solvent front reached the bottom of the paper (descending partition), the chromatogram was air dried, sprayed with a solution of aniline hydrogen phthalate in butanol saturated with water, and heated at 110° C. for 7–10 min. to develop the spots. Solutions of authentic samples of methylglucoses were similarly chromatographed to identify the spots. For quantitative analyses, guide strips along each side of the main chromatogram were sprayed, after development, to locate each component. The corresponding section of the main paper was then cut out and the methylated sugar eluted with water. The sugar in each eluate was determined by the method of Rebenfeld and Pacsu [10].

Calculations

In the methylation of cellulose xanthic acid, the methoxyl content, M (%), that should be found if replacement is complete can be calculated from the xanthate ratio, X, of the cellulose xanthic acid. Each anhydroglucose unit (162 g.) will have initially X xanthate groups, on the average; therefore, X methoxyl groups after methylation. Since each methoxyl group increases the weight of the anhydroglucose unit by 14 mol. wt. units (net increase —CH_2—), then

$$M = \frac{\text{weight of methoxyl}}{\text{weight of sample}} \times 100$$

$$= \frac{31\,X}{162 + 14\,X} \times 100 \quad (1)$$

If all xanthate groups are esterified instead of being replaced, forming Cell—OCS_2CH_3, the number of methoxyls would be the same, but the per cent would be lower because the unit weight is greater (net increase —CS_2CH_2—). In this case

$$M = \frac{31\,X}{162 + 90\,X} \times 100 \quad (2)$$

If some xanthate groups are replaced and some are esterified, then the amounts of ether-bound methoxyl, M_o, and of ester-bound methoxyl, M_s, can be calculated if the amount of sulfur present as S-methyl groups in the methylated xanthic acid is known. Let Y be the number of xanthate groups that are esterified (per mole of anhydroglucose); then $(X - Y)$ is the number of xanthate groups replaced. The unit weight of the methylated xanthic acid is $162 + (76 + 14)Y + 14(X - Y)$ or $(162 + 14X + 76Y)$. The amount of sulfur is Y moles or 64Y grams. Hence the per cent residual sulfur, S, is given by

$$S = \frac{64\,Y}{162 + 14\,X + 76\,Y} \times 100 \quad (3)$$

Since S can be found by analysis, Equation 3 may be used to find the number of S-methyl groups.

$$Y = \frac{(162 + 14\,X)\,S}{6400 - 76\,S} \quad (4)$$

We are now in position to calculate the amounts of ether- and ester-bound methoxyl (M_o and M_s). The second is readily obtained.

$$M_s = \frac{31}{64}\,S \quad (5)$$

The number of ether-bound methoxyls, *i.e.*, those that replaced xanthate groups, is $X - Y$, or 31 $(X - Y)$ grams per mole of anhydroglucose, and the weight of this unit, as given above, is $(162 + 14X + 76Y)$. Hence

$$M_o = \frac{31\,(X - Y) \times 100}{162 + 14\,X + 76\,Y} \quad (6)$$

If we substitute the value for Y given in Equation 4, we find after simplification

$$M_o = \frac{31}{64}\left(\frac{6400 - 76\,S}{162 + 14\,X}\,X - S\right) \quad (7)$$

From Equations 5 and 7 we obtain the total methoxyl content of the methylated cellulose xanthic acid.

$$M = M_o + M_s = \frac{31}{64} \times \frac{6400 - 76\,S}{162 + 14\,X}\,X \quad (8)$$

If there is no residual sulfur ($S = 0$), *i.e.*, only replacement of xanthate groups, then both Equations 7 and 8 reduce to Equation 1, as they should. If there is only esterification of xanthate groups, then $Y = X$, and Equation 3 becomes

$$S = \frac{64\,X}{162 + 90\,X} \times 100$$

and Equations 5 and 8 reduce to Equation 2.

Conclusions

Cellulose xanthic acid can be obtained from viscose in substantially pure form, free of alkali, without significant loss of xanthate groups. When this material is treated with a methylating reagent (nitrosomethylurethane) in methanol at 2° C., all xanthate groups react. Not all are replaced by methyl groups, however; about 20% remains but is esterified, giving the S-methyl ester of cellulose xanthate. Upon hydrolysis of the cellulose chain to glucose and methylglucoses, the S-methyl xanthate esters split off. This methylation procedure, followed by hydrolysis and chromatographic analysis of the hydrolyzate, can be used, therefore, to locate about 80% of the xanthate groups originally present in the viscose. Because of the known differences in reactivity among the three sites for substitution in each anhydroglucose unit of the cellulose chain, it would be unwise to assume that the 20% of xanthate groups unaccounted for (because of ester formation) was distributed in the same way as the 80%. This method, therefore, cannot be used to determine the location of the xanthate groups in cellulose xanthate nor the relative reactivity toward xanthation of the hydroxyls on the second, third, and sixth carbons of the anhydroglucose unit in cellulose.

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The Determination of Sulfur and Its Compounds in Rayon[1]

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Abstract

The determination of sulfur and its compounds in rayon is described. These sulfur compounds are sulfides, sulfites, xanthates, and sulfates. The methods for the determination of these compounds and elemental sulfur were first applied to standard solutions of these compounds. After it was established that these methods yielded accurate results, they were applied to the determinations in rayon. Apart from these determinations, the sums of some and of all compounds were determined. These determined sums proved to be in good agreement with those calculated from the determinations of the individual amounts, so that it is assumed that all methods yield accurate results when applied to the determinations of the S-compounds in rayon.

Introduction

The sulfur content of rayon is of great importance, not only for the manufacturer, who wants to control his products, but also for the textile industry, where rayon is converted.

On the determination of sulfur and sulfur compounds themselves, numerous publications are known. The communications on these determinations in rayon, however, are rather scarce.

Kleinert, Sieber, and Apuchtin [2] have published a method for the determination of sulfide in rayon which is based on the evolution of hydrogen sulfide by heating the yarn with acid and subsequent spectrophotometric determination as molybdenum blue, as indicated by Bethge [1]. Moreover, the former authors state a method for the determination of the sum of sulfides and reducible sulfur. The yarn is reduced with a mixture of stannous chloride and hydrochloric acid; the hydrogen sulfide formed is determined according to the molybdenum blue method. Although Kleinert et al. published a method for the determination of total sulfur in rayon, they were not able to verify the results of the foregoing methods, since they did not determine sulfate and xanthate in the yarn. Moreover, if sulfite is present, this will also be reduced to hydrogen sulfide by stannous chloride in acid medium, so that this method does not yield an insight into the elemental sulfur content of the sample.

Pinte and Pierret [7] determined reducible sulfur by reduction to hydrogen sulfide with stannous chloride and acid and determination of the hydrogen sulfide evolved according to the methylene blue method.

The aim of our investigation is the specific determination of elemental sulfur in rayon. Since it is necessary to check the results obtained, we were also obliged to determine the compounds of sulfur and the sum of all sulfur, elemental and in compounds.

The methods applied were first tried with standard solutions; all methods yielded accurate results. They were then applied to one sample of unfinished rayon; after that, the scheme of analysis was applied to a number of rayon samples which had been spun for experimental purposes.

The results obtained are interpreted with the aid of statistical test, *viz.*, the *t*-test and the *F*-test. To indicate the precision of the results the standard deviation is used. All procedures are fully given in the appendix.

Experimental

The Determination of Sulfides and Xanthates

A 10 g. sample of rayon was heated with 6 *N* hydrochloric acid to expel hydrogen sulfide and car-

[1] Part of the author's thesis, Dissertation Amsterdam, Free University, 1956.

TABLE I

Compound(s) to be determined	Sample	Method of determination	Results			Combined values		Calculated sum	P (t-test)
			$\bar{X}$	S_x	n	$\bar{X}$	S_x		
Sulfide	10 g.	Destruction by heating with acid. H_2S is absorbed in copper (II) acetate and excess Cu^{+2} is titrated with EDTA.	0.0051% S	0.0007% S	8				
Elemental sulfur	2.5–7.5 g.	Extraction with n-hexane. Elemental sulfur is determined spectrophotometrically in the extract.	0.0238% S	0.0022% S	8	0.0245% S	0.0026% S		
		Extraction with n-hexane. After evaporation the sulfur is reduced to H_2S, which is determined complexometrically.	0.0252% S	0.0029% S	8				
Sulfate	3 g.	Fuming with HCl and ignition of the residue. The ash is reduced to H_2S, which is determined complexometrically.	0.0489% S	0.0021% S	8				
		Treatment of S-free yarn with NaOH and after that fuming with HCl and ignition of the residue. The ash is reduced to H_2S, which is determined complexometrically.	0.0955% S	0.0057% S	8				
Sulfide + sulfur + sulfate	1 g.	Reduction with excess HCl, HI, and H_3PO_2 with respect to yarn, H_2S formed is determined complexometrically.	0.123% S	0.0072% S	11			0.1251% S	0.4
Xanthate	1 g.	Destruction with HCl. H_2S is absorbed in copper (II) acetate and CS_2 in ethanolic KOH. Potassium ethyl xanthate is determined spectrophotometrically.	0.0121% S	0.0005% S	6	0.0121% S	0.0005% S		
	10 g.	As the foregoing, potassium ethyl xanthate now being determined by potentiometric titration with copper (II) acetate.	0.0122% S	0.0006% S	4				
Sulfite	5 g.	Destruction with dilute H_2SO_4 and absorption of SO_2 in H_2O_2. The H_2SO_4 formed is titrated with NaOH.	0.0101% S	0.0008% S	4				
Xanthate + sulfite	10 g.	Destruction with acid. H_2S is absorbed in copper (II) acetate. CS_2 and SO_2 are absorbed in ethanolic KOH. The xanthate and sulfite formed are oxidized to SO_4^{-2}, which is determined complexometrically by way of $BaSO_4$.	0.0229% S	0.0008% S	8			0.0222% S	0.2
Sulfide + sulfur + sulfate + xanthate + sulfite	1 g.	Oxidation with Na_2O_2 in a Parr-bomb to SO_4^{-2}. Sulfate is reduced to H_2S, which is determined complexometrically.	0.152% S	0.0066% S	8			0.1473% S	0.01–0.05

$\bar{X}$ = average result. S_x = standard deviation of X. n = number of determinations. P = probability found by applying the t-test.

bon disulfide. These gases were absorbed in copper (II) acetate and ethanolic potassium hydroxide, respectively. After removal of copper sulfide from the copper (II) acetate solution, the excess copper (II) was titrated with the disodium salt of ethylenediamine tetraacetic acid (EDTA) (Procedure 1). Xanthate was determined in the ethanolic potassium hydroxide solution by potentiometric titration of the potassium ethyl xanthate formed with copper (II) acetate (Procedure 2).

When starting from a 1 g. sample, xanthate can also be determined U.V.-spectrophotometrically by an absorption measurement at 301 mμ (Procedure 3).

The results are given in Table I, where $\overline{X}$ is the average result of n determinations, S_x is the standard deviation of one determination, and P is the probability found by application of the t-test. In Table I, all results are given in % S.

From Table I it is seen that the determination of sulfide is well reproducible. No significant differences are found between the results of the two methods for the xanthate determination; neither do their precisions differ significantly. Therefore, results of the methods were combined in order to obtain a better estimate of $\overline{X}$.

The Determination of Elemental Sulfur

Amounts of yarn varying from 2.5 to 7.5 g. were extracted with n–hexane in a Soxhlet apparatus. For 2.5 g. of yarn of this particular brand, the extraction proved to be complete after 1 hr. The completion of the extraction was checked with Sommer's test on elemental sulfur [3, 8] by shaking about 100 mg. of the extracted yarn with 3 ml. of pyridine and 3 ml. of 30% NaOH. This reaction proved to be rather selective; only elemental sulfur and sulfur from polysulfides are detected in this way. Although we have not been able to prove that n–hexane does extract elemental sulfur occluded in the yarn, the conditions of Sommer's test are such as to make it plausible that a negative Sommer reaction means that the extraction of elemental sulfur is complete.

Sixteen extractions and subsequent determinations were carried out. In eight cases sulfur in the extract was determined U.V.-spectrophotometrically by absorption measurement at 276 mμ (Procedure 4). In eight other cases the extract was evaporated to a volume of about 5 ml. and reduced with a mixture of hydrochloric acid, hydroiodic acid, and hypophosphorous acid, according to Pepkowitz and Shirley [6]. The hydrogen sulfide formed was determined complexometrically (Procedure 5).

The results of these two methods are summarized in Table I. Neither in the results nor the respective standard deviations can any significant difference be detected. The $\overline{X}$-values, therefore, were combined in order to obtain a better estimate of $\overline{X}$.

The Determination of Sulfates

Before sulfates can be determined, sulfides, xanthates, and sulfur must be removed. In a platinum dish 3 g. of extracted yarn was fumed with concentrated hydrochloric acid and the residue was ignited. The ash was reduced with the mixture of HCl, HI, and H_3PO_2, and the hydrogen sulfide formed was determined complexometrically. Eight determinations were carried out. The results are given in Table I; the precision is fair.

The Determination of the Sum of Sulfides, Sulfates and Sulfur

One gram of yarn was reduced with the mixture of HCl, HI, and H_3PO_2, and the hydrogen sulfide formed was determined complexometrically (Procedure 8). In this way xanthates are not codetermined: they are decomposed to form carbon disulfide, which is not reduced. In this determination an excess of the reducing mixture (with respect to yarn) had to be used. Eleven determinations were carried out; the average result is given in Table I.

When this result is compared with the sum of the individual amounts of sulfides, sulfur, and sulfates, calculated from the amounts which were determined as described in the preceeding sections, 0.0785%, it is seen that a rather great difference (0.0445%) between the determined sum and the calculated one occurs.

It is remarkable that this deficit is of the same order of magnitude as the amount of sulfate found, 0.0489%. Since the yarn proved to contain an amount of acid it was assumed that part or all of the sulfate was present as hydrogen sulfate. In order to verify this assumption the sulfate determination was repeated with another way of sample preparation.

The extracted yarn was heated gently with dilute sodium hydroxide and fumed with concentrated hydrochloric acid (Procedure 7). After this the

sulfate was determined as described in Procedure 6; eight determinations were carried out, and the results are summarized in Table I. By comparing the calculated sum of sulfides, sulfur, and sulfates by means of the *t*-test, a probability greater than 0.1 is found, i.e., there is no reason to assume a significant difference between the calculated and the determined sum.

The fact that after the NaOH treatment an amount of sulfate is found which does not significantly differ from twice the amount of sulfate found without the NaOH treatment indicates that in this sample sulfate is present in the form of hydrogen sulfate.

The Determination of Total Sulfur

The destruction of yarn by heating with alkaline peroxide, as suggested by Kleinert and coworkers [2] proved to be far from complete and very time-consuming. The destruction, therefore, was carried out with sodium peroxide in a Parr bomb. For this special purpose a macro bomb was constructed (Figure 1). The bomb was made from 18–8 chromium-nickel steel and provided with a nickel coating in order to prevent attack of the bomb when the melt was dissolved. With this bomb 1 g. of yarn was destroyed with 10 g. of Na_2O_2; the sulfate formed was determined by reduction to hydrogen sulfide and complexometric determination of the latter (Procedure 10). The average result of eight determinations after subtraction of the blank is given in Table I; the standard deviation found is satisfactory. When this result is compared with the sum of the S-components determined separately, again a significant difference is found (0.0148%).

This deficit proved to be caused by the fact that, aside from the S-compounds mentioned, another S-compound which yields sulfur dioxide when treated with acid is present in this sample of yarn. Evidence for this fact was obtained from the following experiments.

a. The gases evolved when yarn was heated with acid were first passed through an acid solution of copper (II) acetate, then through a solution of fuchsin or a solution of malachite green. In both cases a decoloration was observed.
b. After passing through an acid copper (II) acetate solution, as described under (a), the gases were passed through a neutral solution of barium chloride. This solution was slightly acidified and heated. After cooling, a precipitate of barium sulfate was observed.

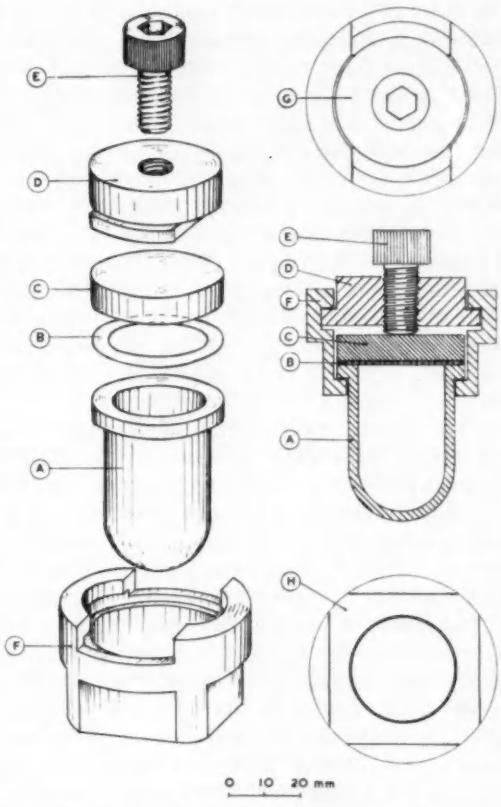

Fig. 1. Parr bomb. (A) nickel coated, 2.5 mm. stainless steel bomb; (B) 0.2 mm. aluminum gasket ring; (C) 8 mm. stainless steel lid; (D) stainless steel tightening plate; (E) screw; (F) stainless steel bayonet coupling; (G) top view of assembled apparatus; (H) bottom view of assembled apparatus.

In both (a) and (b), carbon disulfide does not give any reaction.

c. In the determination of xanthate according to Procedure 2, the alcoholic solution of potassium ethyl xanthate and potassium hydroxide was oxidized with alkaline peroxide. The sulfate formed was determined by precipitation as $BaSO_4$ and titration of the excess Ba^{+2} with EDTA, according to Wilson et al. [9]. The average result of eight determinations is given in Table I.

In order to discover which compound in the yarn yields SO_2 by treatment with acid, three possibilities must be considered—sulfites, thiosulfates, and SO_2 formed by the presence of chemisorbed oxygen on the surface of elemental sulfur. However, in the latter case sulfurous acid will be formed, due to the great solubility of SO_2 in water. Thus, only two possibilities remain—sulfites or thiosulfates. Since 60% of the sulfur present in thiosulfates is reduced by a mixture of HCl, HI, and H_3PO_2, the determination of the sum of sulfides, sulfur, and sulfates (Procedure 8) should yield high results, if SO_2 were present as thiosulfate. This fact was not established (see Table I); we therefore assume the presence of sulfites in this sample of yarn.

Sulfur dioxide, evolved from yarn treated with acid, can be determined by absorption in slightly acid hydrogen peroxide and titration of the sulfuric acid formed. Hydrogen sulfide is then oxidized to sulfur, yielding no hydrogen ions. Carbon disulfide does not interfere. The recovery of this determination (Procedure 9) proved to be 77.4%. It is therefore necessary to correct the results obtained by multiplication with 1000/774. According to Procedure 9, four determinations were carried out. The average result is given in Table I. The calculated sum of xanthates and sulfites does not differ significantly from the sum determined. Comparing the sum of all S-compounds calculated from the amounts determined separately with the determined total sulfur content by means of the *t*-test, a probability of less than 0.05 and more than 0.01 is found. Whether this probability is real or not must be established by the application of the methods to more samples of yarn. However, it must be emphasized that the loss of sulfur is only 3.4% of the sum of five components, so that, considering the small amount of sulfur, the calculated sum of all components agrees rather well with the amount determined.

Since the presence of sulfites in the yarn was not expected at all, it had to be established whether the other determinations are interfered with by the presence of sulfites.

Determination of elemental sulfur is not interfered with because of the selectivity of the extraction and the good agreement between the spectrophotometric and complexometric results.

Determination of sulfides was not interfered with, since the evolution of SO_2 preceeds the formation of H_2S. The evolution of H_2S proved to be dependent upon the thickness of the yarn investigated. But even when yarn of low titer was analyzed, the bulk of SO_2 was eliminated from the reaction vessel by the current of nitrogen before it could react with H_2S.

The xanthate determination is not interfered with. In the destruction of the yarn prior to the determination of sulfate, it is possible that during the NaOH treatment some sulfites are oxidized to sulfates. In the following section this subject will be dealt with further.

Application of the Scheme of Analysis to Several Samples of Rayon

In order to establish more fully the accuracy and the precision of the methods and to find out whether the small probability found for the difference between the calculated sum of all components and the determined one is real or not, seven samples of rayon, spun for experimental purposes, were analyzed for sulfides (Procedure 1), sulfur (Procedure 5), sulfates (Procedure 7), xanthates (Procedure 2), sulfites (Procedure 9), the sum of sulfides, sulfur, and sulfates (Procedure 8), and the sum of all five components (Procedure 10).

It may be remarked that Procedures 1–10 are applicable only to yarn which has not been treated with an S-containing finish, since part of this finish may be extracted simultaneously with elemental sulfur and subsequently be reduced to H_2S.

Since some of these samples had been treated with a mixture of carboxy methyl cellulose and glycerol, the extraction of elemental sulfur from these samples had to be carried out with absolute ethanol. In this way the extraction proved to be selective. Sulfur in this extract was determined in the same way as in the n–hexane extract (Procedure 5). A disadvantage of the extraction with absolute ethanol is that this operation is very time-consuming. The extraction of 10 g. of yarn with n–hexane is complete within 6 hr., while the extraction of this amount of yarn with absolute ethanol takes some 24 hr. and, in the case of a high S-content (Table II, Sample 4), may take even 72 hr. It is recommended that the yarn be sampled before the finishing stage, so that the extraction can be carried out with n–hexane. Because of this difficult extraction, it was investigated whether elemental sulfur could be calculated by subtracting the amounts of sulfides and sulfates, determined separately, from the determined sum of

sulfides, sulfur, and sulfates. This proved to be impossible, because in this case sulfates had to be determined in S-containing yarn, and elemental sulfur reacts with NaOH. This NaOH treatment was necessary, as all samples contained small amounts of acid.

The results of these determinations, carried out in duplicate, are summarized in Table II. The standard deviations of the determinations of the individual components, the sum of sulfides, sulfur, and sulfates, and the total amount of sulfur were calculated from the mean range. The standard deviations found were compared with those given in Table I, the *F*-test being applied. Since no probability of less than 0.10 was found, the two standard deviations were combined in order to obtain a better estimate of the real standard deviation.

The sum of sulfides, sulfur, and sulfates and the sum of all components calculated from the determinations of the individual components were compared with the sums determined for each sample by use of the appropriate average values. From the *d*-values so found, $\bar{d}$ for partial sum and total sum were calculated. The $\bar{d}$'s were tested with respect to zero (*t*-test). From the probabilities found it is seen that there is no reason to assume any significant difference between the determined and the calculated totals. The small probability of less than 0.05, found in Table I, must, therefore, be ascribed to chance fluctuations. Consequently, there is no reason to assume that any of the methods of sample preparation are subject to systematic errors. The fact that $\bar{d}$ for partial sum is positive in all cases where sulfites are present may indicate that part of the sulfites have been oxidized to sulfates by treating the yarn with NaOH prior to the sulfate determination.

TABLE II

Sample	Sulfides	Sulfur	Sulfates	$S^{-2}+S+SO_4^{-2}$	d = calc. − found	Xanthates	Sulfites	Total S	d = calc. − found
	% S	% S	% S	% S	% S	% S	% S	% S	% S
1	0.0046	0.016	0.123	0.144	−0.004	0.0198	—	0.162	0.000
	0.0038	0.016	0.117	0.144		0.0200		0.159	
2	0.0040	0.031	0.132	0.156	+0.005	0.0204	—	0.192	−0.001
	0.0030	0.037	0.123	0.162		0.0192		0.180	
3	0.0056	0.008	0.078	0.084	+0.006	0.0118	0.0147	0.111	+0.004
	0.0056	0.010	0.060	0.072		0.0120	0.0141	0.102	
4	0.0038	0.074	0.117	0.174	+0.010	0.0082	0.0159	0.225	−0.008
	0.0034	0.083	0.090	0.177		0.0088	0.0150	0.212	
5	0.0050	0.036	0.057	0.096	+0.002	0.0132	0.0129	0.132	+0.007
	0.0048	0.039	0.063	0.105		0.0140	0.0135	0.111	
6	0.0072	0.006	0.069	0.087	+0.001	0.0054	0.0117	0.108	−0.002
	0.0046	0.007	0.087	0.093		0.0060	0.0120	0.111	
7	0.0024	0.039	0.066	0.117	+0.003	0.0062	—	0.114	0.000
	0.0030	0.041	0.066	0.093		0.0058		0.114	
s	0.0007	0.0028	0.010	0.0080		0.0005	0.0005	0.0081	
S acc. to Table I	0.0007	0.0026	0.0057	0.0072		0.0005	0.0008	0.0066	
P (*F*-test)	>0.10	>0.10	>0.10	>0.10		>0.10	>0.10	>0.10	
combined S	0.0007	0.0027	0.0083	0.0076		0.0005	0.0007	0.0074	
S in mg of S	0.069	0.27	0.25	0.076		0.051	0.033	0.074	
$\bar{d}$					+0.003				+0.0001
P (*t*-test)					0.10				>0.10

Our final conclusion must be that the results of these determinations on different samples confirm the accuracy of the scheme of analysis developed in the preceding sections.

Procedures

1. Sulfides. Place 10 g. of unfinished previously dried yarn in a distillation apparatus according to Figure 2. Connect the apparatus via a splash head with a train of 3 wash bottles, one containing about 25 ml. of 4 *N* H_2SO_4, to trap hydrochloric acid vapor, and two with 25 ml. of 0.02 *N* copper (II) acetate solution containing 120 ml. of 4 *N* acetic acid/l., in that order. Pass a stream of nitrogen through the apparatus. After 15 min., add through the funnel 75 ml. of 6 *N* HCl and heat to boiling. Boil gently for 45 min., disconnect the wash bottles, and interrupt the stream of nitrogen. Transfer the contents of the wash bottles to a 200 ml. volumetric flask and make up to volume with distilled water. Filter the precipitate, rejecting the first 25 ml. of the filtrate. Add to 100 ml. of the filtrate 2 ml. of 1% tartaric acid solution, 100 mg. of murexide indicator (200 mg. of murexide ground with 50 g. of anhydrous NaCl p.a.), and enough 4 *N* ammonia solution to turn the solution green. Then add 3 more drops of 4 *N* ammonia solution and titrate with 0.02 *N* EDTA solution until the color changes to violet.

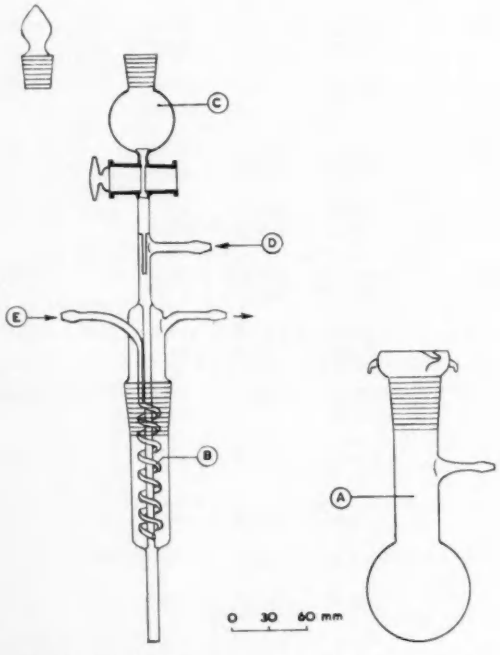

Fig. 2. Distillation apparatus. (A) 250 ml. flask, (B) spiral condenser, (C) funnel, (D) nitrogen inlet, (E) water inlet.

2. Xanthates (potentiometric determination). Place behind the wash bottles in Procedure 1 two other wash bottles each containing 25 ml. of 0.1 *N* ethanolic potassium hydroxide and act according to Procedure 1. Interrupt the stream of nitrogen and transfer the content of the last two wash bottles to a 400 ml. beaker, neutralize with 0.1 *N* acetic acid to pH = 7.0, using a pH meter. Then titrate potentiometrically with 0.02 *N* copper (II) acetate, containing 6 ml. of 1 *N* acetic acid/l., using a copper electrode as an indicator electrode and a saturated calomel electrode as a reference electrode [4].

3. Xanthates (spectrophotometric determination). Place 1 g. of unfinished previously dried yarn in the distillation apparatus (Figure 2) and connect this with three wash bottles, one containing 15 ml. of 4 *N* H_2SO_4 and 15 ml. of 0.02 *N* copper (II) acetate, and two containing 25 ml. of 0.1 *N* ethanolic potassium hydroxide solution, in that order. Pass a stream of nitrogen through the apparatus and, after 15 min., add through the funnel 30 ml. of 6 *N* HCl. Heat to boiling, boil gently for 45 min., disconnect the washing bottles, and interrupt the stream of nitrogen. Transfer the contents of the last two wash bottles to a 100 ml. volumetric flask and make up to volume with distilled water. Measure the absorption of this solution at a wavelength 301 mμ, using 1 cm. cells against a blank, prepared by diluting 10 ml. of 0.1 *N* ethanolic potassium hydroxide with 10 ml. of water. Determine the amount of xanthate sulfur with the aid of a calibration graph, prepared by dissolving known amounts of potassium ethyl xanthate in 0.05 *N* KOH in 50% ethanol and measuring the absorption at 301 mμ in 1 cm. cells [5].

4. Elemental sulfur (spectrophotometric determination). Transfer 10 g. of unfinished previously dried yarn to a Soxhlet extractor.[2] Pour about 225 ml. of n–hexane of spectrograde quality through the extractor into the round bottom flask and heat to boiling. Extract at a moderate rate for about 6 hr. and test for completion by applying Sommer's test.[3] After complete extraction, transfer the yarn to a glass filter, pass the n–hexane extract through the filter, and collect the filtrate in a 250 ml. volumetric

flask. Finally, wash the yarn with several small portions of n–hexane and press out. Preserve the yarn for the sulfate determination according to Procedure 7. Make the filtrate up to volume with n–hexane and measure the absorption of this solution at a wavelength of 276 mμ against a blank of n–hexane, using 1 cm. cells. Calculate the amount of sulfur with the aid of a calibration graph, prepared by dissolving known amounts of sulfur in n–hexane and measuring the absorption as indicated.

5. Elemental sulfur (complexometric determination). Extract 10 g. of unfinished previously dried yarn with n–hexane of analytical grade,[4] filter the yarn, and wash as described in Procedure 4. Place the filtrate and washings in the distillation apparatus (Figure 2) and evaporate until the volume has reduced to about 5 ml. Connect the apparatus via a splash head with 3 wash bottles, the first containing 25 ml. of 4 *N* H_2SO_4 and each of the other two containing 25 ml. of 0.02 *N* copper (II) acetate that contains 120 ml. of 4 *N* acetic acid/l. Act according to Procedure 1; but now add 30 ml. of a mixture of HCl, HI, and H_3PO_2 [6] through the funnel. Heat for 30 min. and determine hydrogen sulfide according to Procedure 1.

6. Sulfates (sodium sulfate). Add 20 ml. of 6 *N* HCl to 3 g. of unfinished previously dried yarn in a platinum dish and evaporate to dryness. Ignite the residue and transfer the ash quantitatively to the distillation apparatus (Figure 2). Evaporate to dryness and reduce the sulfates with 25 ml. of the mixture of HCl, HI, and H_3PO_2 to hydrogen sulfide, according to Procedures 5 and 1.[5]

7. Total sulfates. Add to 3 g. of unfinished previously dried yarn, which is free from elemental sulfur, 20 ml. of 1 *N* NaOH and heat for 10 min. on a steambath. Acidify with 6 *N* HCl and evaporate to near dryness. Repeat this using a total volume of 20 ml. of acid; finally evaporate to dryness. Ignite the residue and determine sulfates according to Procedure 6.

8. Sulfides + sulfur + sulfates. Place 1 g. of unfinished previously dried yarn in the distillation apparatus (Figure 2). Connect the apparatus via a splash head with 3 wash bottles, the first containing 25 ml. of 4 *N* H_2SO_4 and the other two each containing 25 ml. of 0.02 *N* copper (II) acetate which contains 120 ml. of 4 *N* acetic acid/l. Pass a stream of nitrogen through the apparatus and after 15 min. introduce through the funnel 100 ml. of the mixture of HCl, HI, and H_3PO_2, heat to boiling, and boil gently for 30 min. Determine the hydrogen sulfide evolved as described in Procedure 1.

9. Sulfites. Place 5 g. of unfinished previously dried yarn in the distillation apparatus (Figure 2). Introduce into the absorption apparatus (Figure 3) 3 ml. of 30% H_2O_2 and 20 ml. of water, add 8 drops of bromophenol blue solution (1 g. in 15 ml. of 0.1 *N* NaOH, made up with water to 1 l.), and add enough 0.01 *N* NaOH or H_2SO_4 to turn the the solution an intermediate blueish-green color. Then

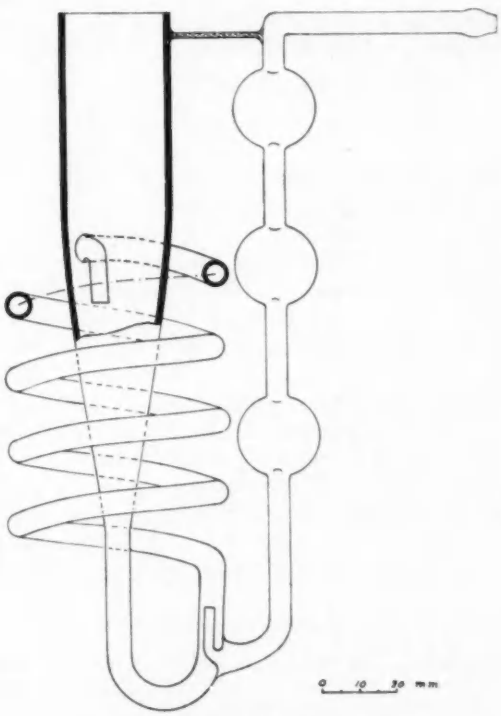

Fig. 3. Absorption apparatus.

[2] When amounts of sulfur over 0.03% are present, it is advisable to start with a smaller amount of yarn, *e.g.*, 4–5 g. The extraction time then will be shorter.

[3] Shake in a test tube about 100 mg. of the extracted yarn with 3 ml. of analytical grade pyridine and 3 ml. of 10 *N* NaOH. No blue coloration should be observed if the extraction is complete.

[4] If absolute ethanol is substituted for n–hexane, the method may be applied to yarn containing finish of carboxy methyl cellulose and glycerol. The extraction with absolute ethanol, however, will—as a rule—take much more time.

[5] This procedure is only applicable to the determination of total sulfate when the sample does not contain acid.

connect the bubbler with the distillation apparatus and pass a stream of nitrogen through the apparatus. After 15 min., introduce through the funnel 150 ml. of 4*N* H_2SO_4 and heat carefully to boiling. Boil gently for 45 min. and without detaching the bubbler or interrupting the stream of nitrogen, titrate the acid formed every 5 min. or so with 0.01 *N* NaOH to the initial intermediate blueish-green. Correct the result for incomplete recovery of SO_2.

10. Total sulfur. Place 1 g. of unfinished previously dried yarn with 10 g. of Na_2O_2 (analytical grade) in the Parr Bomb (Figure 1). Close the bomb, tightening the screw to ensure a gas-tight seal. Place the bomb in an oven and heat over a gas flame of 1 cm. height for 4 min. After cooling for a few minutes immerse the bomb in cold water for a few seconds and allow to cool further to about 50–60° C. Loosen the screw, remove the lid, and carefully rinse the contents with water into a 400 ml. beaker. Boil the solution after addition of 3 drops of 0.05% osmic acid solution until all H_2O_2 has disappeared. Acidify with 4 *N* HCl and transfer the solution to the distillation apparatus. Evaporate to dryness and determine sulfates by reduction to hydrogen sulfide as described in Procedures 5 and 1, using 50 ml. of the reducing mixture according to [6]. Carry out a blank determination on 10 g. of Na_2O_2.

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Properties of Wool Modified with Difunctional Isocyanates

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Abstract

The reaction of wool with toluene-2,4-diisocyanate and hexamethylene diisocyanate is described. The treated wools exhibit greater resistance towards solubilization in hot acid and alkali and towards attack by several other chemical agents. The wet single-fiber stress–strain properties exhibited below 30% extension are only slightly affected by treatment with isocyanates. The values for stress at break and elongation at break, however, are considerably lowered by treatment with difunctional isocyanates, but not with phenyl isocyanate. Fabric stiffness and crease recovery are only slightly affected by the isocyanate pickups studied.

Introduction

The treatment of wool with ethyl, octadecyl, α-naphthyl and phenyl isocyanates and the resulting properties are described in an earlier communication [7]. At low uptakes the modified wools show improved resistance to solubilization in hot acid, whereas at higher pickups greater resistance to attack by alkalies and other reagents is conferred. In this study some chemical and physical properties of wool treated with toluene-2,4-diisocyanate and hexamethylene diisocyanate are compared.

Materials and Methods

The treatment of wool and the methods of testing were, in general, those described earlier [7]. A 6-oz. Botany Style 404 white wool flannel, thoroughly solvent extracted and cut into squares of 2 g. each, was used. The isocyanates were commercial products and used without further purification.[1]

Treatment of Wool

The fabric was dried at 105° C. for several hours and transferred to a round-bottomed flask fitted with condenser and $CaCl_2$ tube. Dry pyridine was added and, when the appropriate temperature was reached, the isocyanate. Eighteen milliliters of pyridine and 2 ml. of isocyanate per gram of wool were used throughout the experiments. At the end of the chosen reaction period the wool was quickly rinsed in dry carbon tetrachloride. The rinse was immediately followed by extraction for 2 hr. with CCl_4 in a Soxhlet apparatus and finally with ethanol for 8 hr. This procedure avoided troublesome deposits otherwise apt to form on the surface of the fabric. After washing for several hours in running water, the samples were conditioned at 21° C. and 65% relative humidity approached from the wet side.

Methods of Testing

1. Acid solubility was determined from weight decrease following immersion of 400 mg. of the flannel in 4 *M* HCl for 1 hr. at 65° C. according to the method adopted by Zahn and Würz [11].

2. Alkali solubility was determined from weight decrease following immersion of the flannel in 0.1 *M* NaOH for 1 hr. at 65° C. according to the method of Harris and Smith [6].

3. Solubility in ammonia after treatment with peracetic acid was carried out according to the directions of Alexander et al. [3]. Four hundred milligrams of wool were treated for 25 hr. with 100 ml. of 2% peracetic acid and finally with 100 ml. of 0.3% ammonia.

Prior to treatment with acid, alkali, or peracetic

[1] Samples of isocyanates were kindly provided by Mobay Chemical Co., St. Louis 4, Mo.; by E. I. du Pont de Nemours and Co., Wilmington, Delaware; and by National Aniline Division, Allied Chemical and Dye Corp., Buffalo, N. Y. Mention of specific products does not imply endorsement by the Department of Agriculture over others of a similar nature not mentioned.

acid, all samples of flannel were unraveled and cut into small pieces to facilitate penetration of the reagent.

4. Felting shrinkage was obtained from area measurements after milling at 1500 r.p.m. for 4.0 min. at 39–41° C. in the Accelerotor [2] with 0.5% sodium oleate, liquor–wool ratio 50/1. Four-inch flannel squares were first protected from raveling by cementing the edges with plastic glue. The squares were relaxed prior to milling by soaking 30 min. in distilled water containing 0.05% Triton X-100, a nonionic detergent, at 40–50° C. Under these conditions, untreated flannel shrank 40% in area.

5. Supercontraction was measured by observing length changes of single fibers exposed to 5% $NaHSO_3$ at 97° C. for 1 hr. [10].

6. Force–extension data were obtained from single fibers submerged in water after removal from the treated fabric samples. Testing was carried out at a constant rate of loading of 2 g./grex/min. based on the average grex of the untreated fiber. Measurements were made on 36 fibers from each treated fabric.

7. Fabric stiffness was determined by the cantilever method according to ASTM specifications [1]. It is considered that differences in flexural rigidity of about 10% can just be detected subjectively.

8. Crease recovery was determined with the Monsanto Wrinkle Recovery Tester by the vertical strip method [2], using a 1.5-lb. weight to crease the fabric. The values presented are the averages for six fabric strips.

Discussion

The conditions required for reaction of the diisocyanates with wool, summarized in Table I, are somewhat more severe than those necessary for reaction of monofunctional isocyanates [7]. Six hours at the reflux temperature of pyridine are needed for a pickup of 8% of toluene diisocyanate. Under similar conditions a pickup of 39% is obtained after treatment of wool for 1 hr. with α-naphthyl isocyanate. Presumably all side chains with reactive hydrogen atoms, namely amino, hydroxyl, thiol, phenolic, amide, guanidino, carboxyl, and imidazolyl groups, are capable of reacting with isocyanates [7]. The tendency of aromatic isocyanates to dimerize in pyridine may be responsible for the observed differences in rates of reaction. Isocyanate dimerization is catalyzed by pyridine, the dimers being often so inert as to permit crystallization from ethanol. At higher temperatures, however, the dimers revert to the more reactive monomers. For example, in the absence of catalyst, the dimer of toluene-2,4-diisocyanate has been reported to dissociate at 150° C. and is almost completely converted to monomer at about 175° C. [4]. However, the reaction of isocyanates with wool is accomplished in the presence of catalyst, so that the concentration of monomer should be appreciable at the reflux temperature of the pyridine. Another explanation for the differences in rates of reaction may be that the isocyanates penetrate the fiber at different rates.

TABLE I. Influence of Temperature and Duration of Heating on the Reaction of Diisocyanates with Wool

Treatment	Temperature, ° C.	Time, hr.	Uptake, %
Toluene-2,4-diisocyanate	97	1.5	1.2
	Reflux	1.0	3.4
	"	2.0	4.6
	"	3.5	6.8
	"	6.0	8.0
Hexamethylene diisocyanate	"	0.5	4.2
	"	0.75	6.0
	"	1.0	9.8
	"	2.0	12.5
	"	7.0	19.0

Some chemical properties of wool treated with toluene diisocyanate and hexamethylene diisocyanate are summarized in Table II. In general, the properties are similar to those of wool modified with monofunctional isocyanates [7]. Marked protection against solubilization in hot acid is found, even at relatively low uptakes. In this respect the difunctional reagents appear slightly superior to the monofunctional isocyanates.

It is noted that treatment with diisocyanates also greatly improves resistance to attack by alkali. Solubility of wool in hot alkali is generally considered to be related in part to the instability of cystine cross-links between polypeptides. These linkages may be replaced with more stable bridges by treating reduced wool with ethylene bromide [9] or *bis*-maleimides [8]. An alternate procedure lies in the introduction of additional cross-links with reagents such as formaldehyde or glyoxal. These treatments generally confer increased resistance to solubiliza-

[2] Purchased from the Atlas Electric Devices Co., Chicago 13, Ill.

tion in hot alkali. It is therefore significant that similar pickups of diisocyanates are more effective than monofunctional isocyanates [7] in conferring resistance towards solubilization in hot alkali.

The decrease in solubility of wool in ammonia after treatment with peracetic acid is sometimes taken as evidence for the introduction of stable cross-links. In our experiments it was found that treatment with pyridine alone lowers the solubility [7]. However, the solubility is lowered somewhat more by treatment with diisocyanates.

Hot sodium bisulfite solution attacks the disulfide bonds of wool, causing the fibers to shorten. This effect, termed supercontraction, is lessened by treatment with monofunctional isocyanates. The introduction of bulky groups may protect the disulfide bonds from attack by the bisulfite. However, the greater protection given by both toluene diisocyanate and hexamethylene diisocyanate supports the hypothesis that, in addition, relatively stable covalent links between polypeptides have been introduced by these reagents.

The felting shrinkage behavior of treated samples is given in Table II. The aliphatic diisocyanate is least effective in reducing felting.

The dyeing characteristics of wool modified with isocyanates show marked changes. Above about 5% pickup of isocyanates studied, the modified wool exhibits marked resistance towards acid dye uptake. Figure I shows samples of goods knitted with alternating bands of yarn, untreated and modified by uptake of 5% of toluene-2,4-diisocyanate before dyeing in the piece with the acid dyes, Brilliant Milling Blue B and Wool Orange GG. A fair degree of resist is evident.

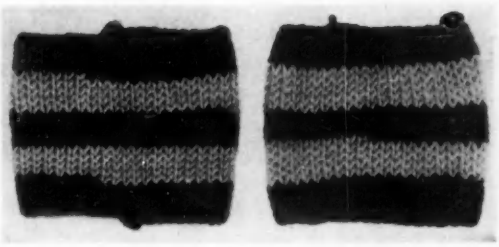

Fig. 1. Samples of goods knitted with alternating bands of yarn, untreated and modified by uptake of 5% toluene-2, 4-diisocyanate before dyeing in the piece with acid dyes.

Wet single fiber stress–strain properties of fibers taken from treated fabrics are summarized in Table III. Below 30% extension the properties are only slightly affected by treatment with pyridine alone or with the isocyanates. There would appear to be a slight increase in the initial modulus for those fibers treated with isocyanates, the effect being most pronounced in the case of phenyl isocyanate. The spread in data is such that an increase in Young's modulus cannot definitely be said to occur. However, isocyanate treated fibers show a small increase in hysteresis in the stress–strain cycle. The treated fibers are somewhat slower in returning to their original length and at zero load are 1 to 2% longer. After a minute's rest under zero load, the fibers regain their original lengths. We conclude that the isocyanate treatment results in a slight stiffening of the fibers at low elongations.

Above 30% extension, however, the fiber properties are noticeably changed by treatment with the two difunctional isocyanates; breaking stress and breaking elongation are considerably lowered. Similar reductions in breaking stress and breaking elon-

TABLE II. Properties of Wools Treated with Diisocyanates *

Treatment	Pickup	Acid solubility	Alkali solubility	Peracetic acid-NH_3 solubility	Super-contraction	Shrinkage	Regain
Untreated	0	8.8	12.4	83	27	40	14.4
Pyridine alone, refluxed 3 hrs.	−1.0	8.8	12.8	55	27	40	14.0
Toluene-2,4-diisocyanate	3.4	2.2	6.6	46	8	16	11.5
	8.0	1.0	4.6	16	6	9	10.5
Hexamethylene diisocyanate	4.2	2.1	7.0	33	11	23	12.0
	19.0	0	2.8	2	0	7	9.5

* All values, expressed as per cent of dry weight of wool before treatment, are the averages of at least two determinations.

gation are noted after treatment of wool with formaldehyde [5], which is generally considered an effective cross-linking agent. The introduction of new cross-links into the fiber structure by means of formaldehyde or diisocyanates might be expected to lower the ultimate elongation of the fiber by limiting the uncoiling and slippage of polypeptide chains. On the other hand, cross-linking might also be reasonably expected to increase the ultimate breaking strength instead of giving the observed decreases.

Values for fabric stiffness and wrinkle recovery are summarized in Table IV and reflect the findings that the single fiber stress–strain properties below 30% extension are only slightly changed. It would appear that the fabrics are somewhat stiffer and that the crease recovery is slightly diminished after isocyanate treatment, but the effect is not great.

TABLE III. Comparison of Wet Single-Fiber Properties of Fibers Removed from Treated Fabrics *

Treatment**	Stress at 30% extension, g./gx.	Young's modulus, g./gx.	Stress at break, g./gx.	Extension at break, %
Untreated	0.44±.06	7.6±1.1	0.85±.13	48.2±1.4
Pyridine alone, refluxed 3 hrs.	0.40±.06	7.8±1.2	0.71±.12	45.1±2.7
Phenyl isocyanate	0.43±.05	8.5±0.7	0.78±.10	46.7±2.1
Toluene-2,4-diisocyanate	0.48±.06*	8.1±1.0	0.52±.08	29.6±3.4
Hexamethylene diisocyanate	0.54±.10*	8.1±1.0	0.48±.10	24.9±5.0

* Figures are the averages of at least 36 determinations except where an asterisk indicates that only 20 fibers withstood the elongation. Values are given in terms of 95% confidence limits.

** The isocyanates were applied to give 5% uptakes.

Summary

Relatively low pickups of diisocyanates significantly protect wool towards solubilization in hot acid or alkali. The marked protection towards solubilization in alkali is taken as evidence for the introduction of relatively stable cross-links into the wool structure.

Differences in the rates of reaction of isocyanates with wool may be due in part to reversible dimerization of the reagents in the pyridine solvent. Possible differences in rates of diffusion of the reagents into the dry fiber may provide another explanation of the differing reactivities.

The wet fiber properties exhibited below 30% extension are only slightly changed by treatment with pyridine or isocyanates. The values for stress at break and elongation at break, however, are considerably lowered by treatment with difunctional isocyanates, though not with phenyl isocyanate. Fabric stiffness and crease recovery are changed very little by the isocyanate pickups studied.

Increased resistance to acid dye uptake is noted for wools treated with either mono- or difunctional isocyanates.

TABLE IV. Properties of Fabrics Treated with Isocyanates *

Treatment	Stiffness: Bending length, cm. Warp	Stiffness: Bending length, cm. Fill	Stiffness: Flexural rigidity, mg.-cm. Warp	Stiffness: Flexural rigidity, mg.-cm. Fill	Stiffness: Flexural rigidity, mg.-cm. Overall	Crease recovery, % Warp	Crease recovery, % Fill
Untreated	1.58	1.52	82	74	78	85	82
Pyridine alone, refluxed 3 hrs.	1.67	1.53	98	75	86	77	76
Phenyl isocyanate	1.57	1.52	86	78	82	79	78
Toluene-2,4-diisocyanate	1.63	1.54	95	81	88	78	77
Hexamethylene diisocyanate	1.62	1.53	94	80	87	79	78

* The presented values are the averages for six fabric strips. The isocyanates were applied to give 5% uptakes.

Acknowledgments

The authors express appreciation to Dr. Harold P. Lundgren for his guidance and encouragement, to Mrs. Lura Brown for performing some of the physical measurements, and to C. E. Pardo for the shrinkage tests.

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Evaluation of Soil Removal from Cotton Fabrics

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Abstract

Certain characteristics of a soil-fiber complex are critically important to valid comparison of the relative soil removal abilities of washing machines and detergents. These characteristics, stated herein, are obtained by a method of direct precipitation of zirconyl phosphate soil in cotton fabric. Soiled test cloths thus prepared permit evaluation of soil removal with a high degree of precision and reproducibility.

Introduction

This paper describes a soil removal test based on the concept that a single, solid, submicron soil precipitated in cotton fabric can be used validly to evaluate soil removal ability. This test is designed primarily for evaluation of soil removal by washing machines and for a study of the sensitive factors involved in washing. It also discriminates detergent abilities to remove ingrained solid soils.

Requirements

Limitations of other methods are amply described in the literature [1, 4, 7, 8]. They serve to emphasize the necessity that rigid requirements be met, according to concept, in the preparation of soil test cloths. These requirements are:

1. A solid submicron soil must be in intimate contact with the fine surface structure of fibers or lodged in interfiber spaces, so that measurement of soil removal reflects properties of both soil and fiber. This condition is referred to as a soil-fiber complex.
2. The soil particles must be randomly distributed among the fibers so that there is no uneven retention or pile-up of soil. Also there must be no fractionation of particle sizes in respect to depth of penetration of the soil into the fabric.
3. The soil must be inert to chemical reaction with detergent compounds.
4. Soil measurements must relate to the quantity of soil within the fabric.

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5. Soil particle size must be controlled by the method of application.

Characteristics of Method

In this investigation, the foregoing requirements are met to a high degree by a method of direct precipitation of an extremely insoluble substance, zirconyl phosphate, in the fabric. A soil-fiber complex is thus obtained with high but discriminating resistance to soil removal. The resulting particles are submicron (see Figure 1), and randomly distributed over the fiber surface. Particle size is found to be adequately controlled by close conformity to the soiling procedure. Control of particle size is important in achieving reproducibility of soil removal values.

Redeposition is effectively eliminated by use of a relatively infinitesimal amount of soil together with large amounts of water and cloth in the washing process.

In relating the soil measurement to the quantity of soil within the fabric, zirconyl phosphate is advantageous because radiotracer Phosphorus 32 can be readily incorporated as phosphate to constitute an integral part of the single soil. The beta radiations are sufficiently penetrating to permit measurement of deeply ingrained soil.

Validity of Method

While precision and reproducibility of this method may be judged from the test results, it is improbable that proof of validity of this or any method of evaluation of soil removal ability can be given by a single critical set of experiments. As has been reported by Köhler [5], a soil removal test, to be valid, must subscribe to general experience that longer wash times, higher temperatures, and increased mechanical action produce greater soil removal. Comparison to practical wash tests is unwieldy, however, because in such tests questions arise as to a representative soil and the ability to measure precisely the per cent soil removal of an ingrained soil. At best, in practical tests, much replication is required to distinguish large differences.

Where direct proof of validity cannot be obtained, often the assembling of all experiments into an entirely consistent and logical pattern offers substantiation of a method. Factors such as time, temperature, detergent, detergent concentration, agitator speed, water–load ratio, etc., are examined and their effects and interactions with each other ascertained. It is strong support of validity for a soil removal method to withstand contradiction when examined over wide ranges of these interacting sensitive factors.

The use of different types of cotton cloth or different particle sizes in the soil-fiber complex will change the magnitude of soil removal responses; if the test is valid, the ranking of washing machines or detergents will remain unchanged.

However, the ranking of detergents, and possibly washing machines, may change at very different levels of sensitive variables. For instance, a detergent superior in soft water may be inferior in hard water. For this reason a simple rating may be misleading even when the conditions of test are closely defined.

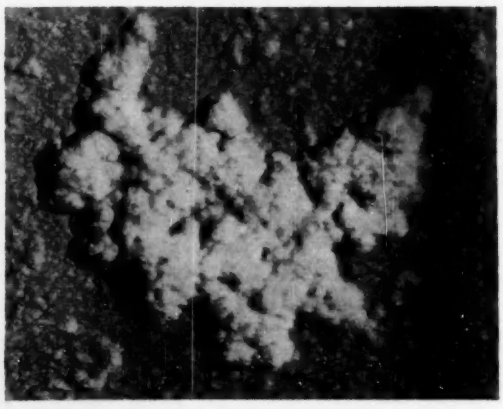

Fig. 1. Flocculated zirconyl phosphate (1 μ), precipitated in aqueous solution and isolated after 1 wk.

Statistical Experiments

The large number of sensitive variables involved in soil removal and the significance of their interactions almost compel the use of methods of statistical factorial design and analysis of variance. These methods are, in general, objective and economical.

In applying analysis of variance to washing machine investigation, it should be noted that the soiled test swatches, from which measurements are made, quickly become randomized in the washing process and permit an independent value of soil removal to be obtained from each soiled swatch. Replication, resulting from the large number of swatches generally used, permits a high degree of test significance, provided variability is small.

The *F*-test in statistical analysis is well suited for a comparison of the mean values of soil retention tests. It must be emphasized, however, that adverse loading conditions—for instance, extremely low water–load ratio—may effect randomness of distribution of swatches and validity of tests.

Procedure

Preparation of Swatches

White bleached Indian Head cloth (Nashua Mills Manufacturing Co.) is cut from the bolt into 22 in. strips and washed with 0.24% built detergent and 150° F. soft water in an agitator type washing machine. The wash and five subsequent soft water rinses are each of 15 min. duration. The cloth is spun to remove excess water and ironed to dryness without stretching the fabric. It is then cut to swatch size, 3 × 5 in., using pinking shears, and stored 12–48 hr. at 100° F. Sufficient swatches are prepared at one time for a complete series of tests. Before they are soiled, the swatches are carefully marked to designate the center of the soil spot and to align them reproducibly with respect to the counter. Figure 2 shows swatch, sample holder, and counter.

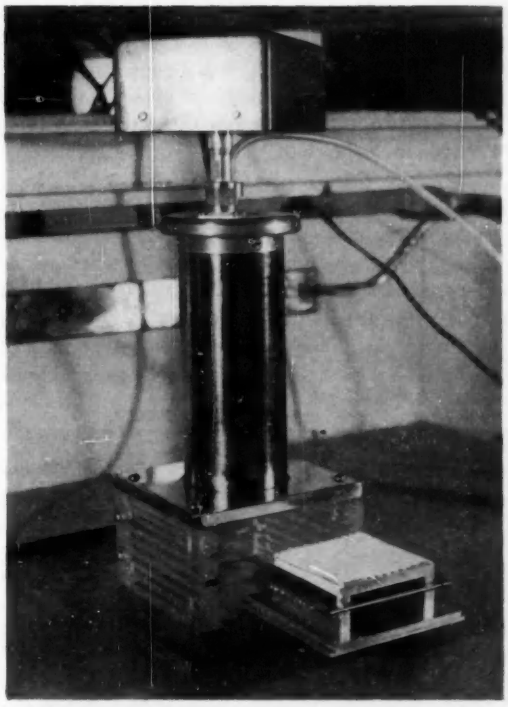

Fig. 2. Proportional counter with switch on stage.

Soiling Process

Zirconyl phosphate soil [6] is constituted from two soiling solutions, 0.66 *M* $ZrO(NO_3)_2$ and 0.15 *M* K_2HPO_4, the latter containing sufficient radiotracer P^{32}, as phosphate, to approximate 100,000 c./min. on initial count of the soil spot.

In the soiling process, a swatch is placed, marked side up, over a beaker and 100 λ of K_2HPO_4 solution is rapidly discharged from a pipette in contact with the center mark. It is important that the K_2HPO_4 be applied first. Exactly 20 sec. later, 400 λ of $ZrO(NO_3)_2$ is discharged from a second pipette without touching the tip to the cloth. One minute later the swatch, on a suspending clip, is immersed in a 75° F. unstirred deionized water bath. It is soaked 10 min., removed, allowed to drip free of excess water, and suspended 16–60 hr. in a drying oven at 125° F. These operations can be synchronized to a high degree of efficiency and will produce a soil of about ½ in. diameter. A small amount of the soil is carried farther from the center (see Figure 3). The particle sizes resulting from this method of precipitation are well under one micron. When such soil is precipitated in water and dialyzed to remove electrolytes, it can be suspended in an Andreason pipette at least one week with no observable settling.

Counting of Radioactivity

The swatches are randomized, apportioned into sets of ten, and numbered. Just before washing, a set of ten is counted by means of proportional counting equipment. A 3-min. count is taken, and swatches deviating from the mean count by more than 10% are rejected and replaced. It is a sound precaution to calibrate every set of ten measurements by means of a standard.

This investigation used a Nuclear Instrument and Chemical Corp. Ultrascaler, set at 2200 volts, and a D-47 Counter with "P" gas for counting purposes.

Washing Method

Soft water is used throughout, except in tests involving quality of water. The detergent is dissolved in 3 gal. of water at 5–10° F. above the specific test

temperature. It is then added to the washing machine, and the test water level is adjusted at a temperature 2° F. above the test temperature. The wash water is agitated briefly to obtain uniformity of temperature and detergent. These preparations are made while the cloth load is being assembled.

Thirty-four "stuffers," 21 × 35 in., which have been cut from Indian Head and hemmed, constitute a 7 lb. washing machine load. The load includes ten special stuffers, which have open and hemmed center sections, 1½ × 2 in., termed "windows," across which the counted swatches are stapled (see Figure 4). The stuffers, including the special ten, are randomized and placed in the washing machine as quickly as possible. The above operations should rapidly follow the counting procedure. Unless otherwise specified, a complete washing cycle, including rinses and spin drying, is carried out.

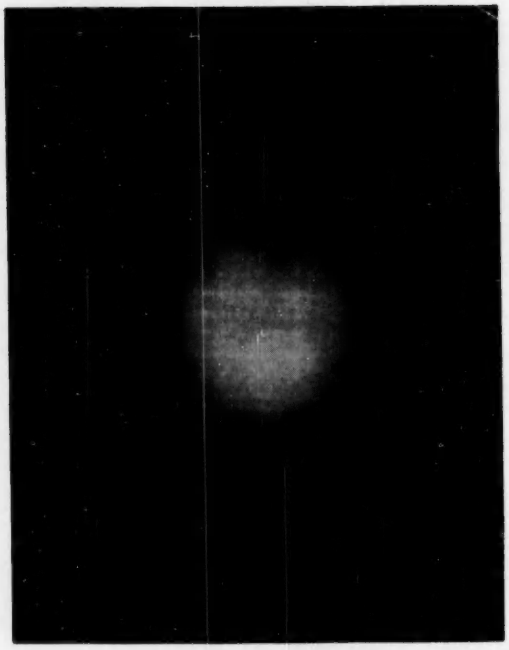

Fig. 3. Autoradiograph of zirconyl phosphate soil precipitated in Indian Head; magnification 2.5 ×.

Final Procedure

The swatches, when removed from the stuffers and dried 10 min. in a dryer, are ready for recount of radioactivity under exactly the same conditions as the initial counting. Correction is made for decay of P^{32}, and per cent retention (100 times the final count divided by the initial count) of the zirconyl phosphate is calculated. Results for the 10 randomized test swatches are treated as 10 independent values. The mean, standard error, and 95% confidence limit for the test are recorded.

Precautions

Radiophosphorus on swatches is handled safely and routinely at the test concentrations if minimal precautions, such as good housekeeping practices, are followed. All transfer and soiling operations are carried out in radiochemical fume hoods.

Detergents sometimes vary from box to box; therefore, the amount of detergent material needed for a complete series of tests is measured out beforehand, mixed thoroughly, and stored in a closed container.

Stuffers are reused in subsequent washing tests. However, it is recommended that they be given 5 complete rinses of 15-min. duration in soft water and stored dry.

New stuffers should be given at least 5 complete washings to remove excess lint before using.

Experiments and Discussion

Representative experiments are reported in this section to demonstrate application of the method and permit examination of reproducibility, precision, and

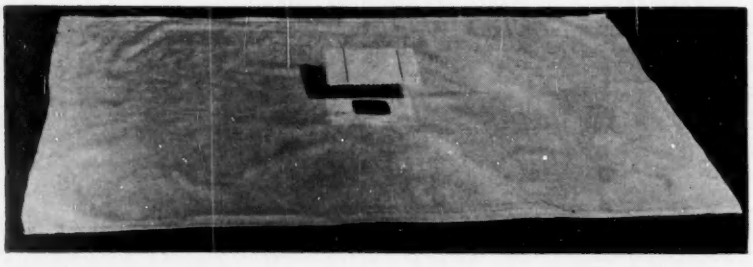

Fig. 4. Soiled swatch above special stuffer with window.

validity. Precision refers to dispersion of soil removal responses about the mean; reproducibility refers to the ability to duplicate mean values with change of time, place, personnel, batches of soil, etc.

Table I-A lists a sequential factorial experiment (method given in Davies [2]), and Table I-B gives the soil retention values obtained. The 48-block experiment, examining four factors at two levels and one factor at three levels, was conducted over a period of two weeks. Soiling solutions were reconstituted three times during the course of experiment, providing an implicit but severe test of reproducibility.[2]

[2] The experiment, although presented for compactness as Table I-B, was analyzed as three separate 5-factor, 2-level (2^5) blocks with overlapping responses. Temperature levels for the three blocks were 100° and 125° F., 125° and 150° F., and 100° and 150° F. respectively.

This was a sequential factorial experiment in the sense that later tests were added to previous tests and then analyzed. In other words, testing was done at 100° F. and 125° F., randomizing the time element in filling in the blocks. Later, testing was done at 150° F.

The ability to add later tests, as experience dictates, is an attribute of the 2^x or 3^x type of design. This is possible if satisfactory reproducibility, as defined here, can be obtained. Accordingly, it was necessary to determine whether the effects of time lapse and different batches of soiling solution

TABLE I-A

Factor	Designation	Levels
1. Temperature	*A**	100° F. 125° F. 150° F.
2. Agitator speed	*B*	45 strokes (oscillations)/min. 68 strokes/min.
3. Wash time (not including rinse time, kept constant)	*C*	10 min. 20 min.
4. 0.25% detergent	*D*	A built nonionic liquid detergent. A built nonionic solid detergent.
5. Water-load ratio	*E*	**Low ratio: 10 gal. water to 7 lb. cloth. High ratio: 17 gal. water to 7 lb. cloth.

* The letters, *A*, *B*, *C*, *D*, *E* refer to the effect in going from a lower level to a high level of each factor, 1, 2, 3, 4, 5, respectively. For example, *B* means the effect on soil retention in going from 45 to 68 strokes/min.

** The low water-load ratio is an extremely adverse condition that tests the versatility of the method.

TABLE I-B

		Low water-load ratio				High water-load ratio			
		Liquid detergent		Solid detergent		Liquid detergent		Solid detergent	
		10 min. wash	20 min. wash	10 min. wash	20 min. wash	10 min. wash	20 min. wash	10 min. wash	20 min. wash
100° F.	45 strokes/min.	83.53% ±0.90% S_x=0.40%	83.10% ±1.04% S_x=0.46%	83.27% ±1.99% S_x=0.88%	79.56% ±1.54% S_x=0.68%	81.85% ±1.07% S_x=0.47%	80.25% ±1.78% S_x=0.79%	78.31% ±1.36% S_x=0.59%	76.73% ±1.29% S_x=0.57%
	68 strokes/min.	81.21% ±1.20 S_x=0.53	80.04% ±1.79 S_x=0.79	80.23% ±1.67 S_x=0.74	77.23% ±1.36 S_x=0.60	79.54% ±1.55 S_x=0.69	73.79% ±0.84 S_x=0.36	77.60% ±0.58 S_x=0.25	73.27% ±0.92 S_x=0.40
125° F.	45 strokes/min.	81.72 ±1.49 S_x=0.66	81.26 ±1.02 S_x=0.45	81.86 ±1.40 S_x=0.62	79.88 ±1.90 S_x=0.84	80.80 ±1.34 S_x=0.60	77.26 ±1.20 S_x=0.52	78.04 ±1.67 S_x=0.74	74.61 ±1.01 S_x=0.45
	68 strokes/min.	80.40 ±1.42 S_x=0.63	77.26 ±1.36 S_x=0.60	78.50 ±1.33 S_x=0.59	74.60 ±0.61 S_x=0.27	76.89 ±1.15 S_x=0.50	73.03 ±0.88 S_x=0.38	75.01 ±0.98 S_x=0.43	71.15 ±0.63 S_x=0.28
150° F.	45 strokes/min.	77.89 ±0.81 S_x=0.36	76.28 ±1.20 S_x=0.53	77.34 ±1.31 S_x=0.58	75.21 ±0.81 S_x=0.36	78.38 ±0.85 S_x=0.37	77.09 ±1.09 S_x=0.47	76.76 ±0.90 S_x=0.40	74.40 ±0.79 S_x=0.34
	68 strokes/min.	76.10 ±0.75 S_x=0.33	74.10 ±1.67 S_x=0.74	75.43 ±1.22 S_x=0.54	72.00 ±1.47 S_x=0.65	73.81 ±0.80 S_x=0.346	70.49 ±0.85 S_x=0.37	72.55 ±0.79 S_x=0.35	69.76 ±0.81 S_x=0.35

For those unfamiliar with the statistical analysis, the effect -1.70% for A as listed in Table I-C means that the soil retention was decreased 1.70% in going from 100° F. to 125° F. The mean square 23.15 indicates that the effect was significant for the set of conditions encompassed by the experiment and not due to error.

were significant. There are many methods, including replication, to determine these significances.

It was felt that the analyses of the experiment as three 2^6 designs would be sufficient for determinations of significance and would present ample contradictions if effects of time and batches were significant. Also, experience shows that laboratory technicians can work out the analysis for 2^x designs in any combination chosen for consideration. If satisfactory reproducibility is ascertained, a $2^4 \cdot 3$ analysis presents the fullest probe into significance of the 5 factors involved.

Figure 5, derived from Tables I-B and I-C, illustrates the meaning of 2-factor interactions. Divergent and increasing effects are positive. Convergent and decreasing effects are positive. Divergent and decreasing effects are negative. Convergent and increasing effects are negative. For example, an examination of the plots relating detergent and temperature in Figure 5 shows that this particular interaction AD is positive from 100° F. to 150° F. Table I-C lists AD as not significant from 100° F. to 125° F. or from 125° F. to 150° F., but significant from 100° F. to 150° F.

By means of the above type experiment the phenomenon of soil removal can be explored over a large number of sensitive variables, adding more to the experimental design as required. Retaining the

TABLE I-C. Analysis of Variance for Experiment 1

	100° F. to 125° F.		125° F. to 150° F.		100° F. to 150° F.	
Combination	Effect	Mean square	Effect	Mean square	Effect	Mean square
A	−1.70%	23.15*	−2.80%	62.50*	−4.49%	161.55*
B	−3.27	85.48*	−3.60	103.90*	−3.30	87.19*
AB	−0.31	0.74	−0.03	0.01	−0.34	0.91
C	−2.86	65.31*	−2.69	58.00*	−2.53	51.31*
AC	−0.16	0.21	+0.33	0.87	+0.17	0.22
BC	−0.77	4.73*	−0.60	2.83†	−0.70	3.99*
ABC	+0.10	0.08	+0.07	0.04	+0.18	0.25
D	−2.00	32.11*	−1.61	20.67*	−1.74	24.12*
AD	+0.13	0.14	+0.26	0.56	+0.40	1.28†
BD	+0.19	0.27	−0.03	0.01	+0.36	1.05†
ABD	−0.39	1.24†	+0.18	0.26	+0.07	0.04
CD	−0.36	1.06	−0.29	0.67	−0.38	1.18
ACD	+0.09	0.07	−0.02	0.00	+0.07	0.04
BCD	+0.22	0.39	+0.08	0.05	+0.21	0.35
ABCD	−0.14	0.15	0.00	0.00	−0.14	0.15
E	−3.47	96.40*	−2.49	49.40*	−2.37	45.03*
AE	−0.12	0.11	+1.10	9.70*	+0.98	7.74*
BE	−0.18	0.26	−0.73	4.23*	−0.82	5.40*
ABE	+0.10	0.07	−0.64	3.32†	−0.55	2.38*
CE	−0.64	3.24*	−0.36	1.06	−0.35	0.97
ACE	−0.02	0.00	+0.29	0.66	+0.27	0.60
BCE	−0.19	0.29	+0.19	0.30	−0.47	1.74†
ABCE	+0.67	3.60*	−0.29	0.66	+0.38	1.17†
DE	−0.33	0.87	−0.33	0.85	−0.24	0.46
ADE	−0.09	0.07	+0.10	0.07	0.00	0.00
BDE	+0.60	2.87*	+0.52	2.19†	+0.51	2.04*
ABDE	+0.02	0.01	−0.10	0.08	+0.22	0.37
CDE	+0.56	2.51*	+0.24	0.44	+0.50	2.00*
ACDE	−0.26	0.55	−0.06	0.03	−0.32	0.83
BCDE	−0.06	0.03	+0.11	0.09	+0.17	0.22
ABCDE	−0.05	0.02	+0.21	0.37	+0.16	0.20
Remainder		0.31		0.24		0.27

Degrees of freedom of each combination = 1.
Degrees of freedom of remainder = 288.

* Denotes significance to 99% level, *F*-test.
† Denotes significance to 95% level, *F*-test.

It is noteworthy that the choice of a wide range of a factor (viz., temperature, 100° F. to 150° F.) produces large effects and interactions (except where maxima and minima are involved) and often shows small interactions to be significant.

breadth of the exploration, the method is highly practical for the ranking of washing machines and detergents.

Particle size of zirconyl phosphate strongly influences the per cent soil retention and must be controlled to achieve a high degree of precision and reproducibility. Particle size can be fairly well controlled by the precipitation method. It is found that the particle size produced as described under Procedure (and here termed C) gives optimum precision. However, if 0.025 *M* K_2HPO_4 and 0.11 *M* $ZrO(NO_3)_2$ solutions, instead of 0.15 *M* and 0.66 *M* respectively, are pipetted on the swatch, a smaller particle size (termed 1/6 C) results. This was experimentally verified by nephelometric measurements which qualitatively related particle size to amount of light scattering. When the 1/6 C soil is used, it is found that per cent soil retention, precision, and reproducibility are decreased.

It is important for validity that no change in the order of ranking of washing machines or detergents should result from change in particle size. For this reason, the experiment reported in Table I was repeated at 100° F. and 150° F., this time using particle size 1/6 C. All the main effects were significant to the 99% confidence level and the directions (signs) of the effects were the same as C. Fewer interactions, however, were significant than with C because of the expected increased error. If the 45 and 68 strokes/min. agitator speeds can be construed as representing two separate washing machines, the effects of agitation and detergent strongly indicate that the ranking of washing machines and detergents by this method are independent of the particle sizes of ingrained soils.

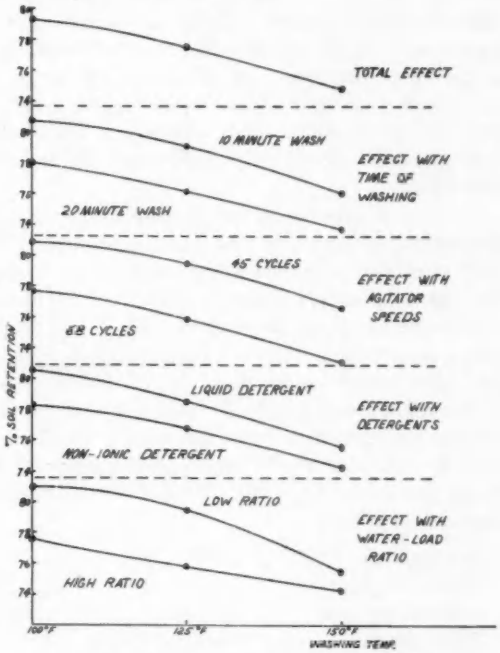

Fig. 5. Temperature effect and interactions.

TABLE II

B = Calcium content in gr./gal. $CaCO_3$

A = Concentration of detergent, %	0	4.5	9	13.5	18	36
0	87.30±2.01% S_x=.89%	94.14±2.13% S_x=.94%	93.71±.84% S_x=.37%	93.88±1.02% S_x=.49%	93.40±.59% S_x=.26%	96.26±1.02% S_x=.45%
.025	77.83±1.54 S_x=.68	89.06±1.31 S_x=.58	91.92±.84 S_x=.37	92.68±1.25 S_x=.61	92.15±.96 S_x=.47	94.25±1.22 S_x=.54
.050	76.91±1.27 S_x=.56	83.62±1.56 S_x=.69	88.52±.61 S_x=.27	91.1±2.26 S_x=1.00	92.92±1.42 S_x=.68	93.28±1.23 S_x=.59
.075	75.76±.77 S_x=.34	77.64±.75 S_x=.36	85.95±.88 S_x=.42	89.02±1.15 S_x=.51	89.73±1.09 S_x=.52	93.16±1.02 S_x=.49
.100	73.66±1.18 S_x=.52	75.71±1.57 S_x=.75	85.61±1.43 S_x=.70	86.06±1.23 S_x=.60	88.68±1.16 S_x=.57	91.07±.11 S_x=.05
.150	75.02±.62 S_x=.305	74.93±1.00 S_x=.48	79.71±1.42 S_x=.68	85.06±1.19 S_x=.74	87.36±1.55 S_x=.74	90.99±1.11 S_x=.53
.250	73.84±1.15 S_x=.55	74.82±1.63 S_x=.78	76.24±1.29 S_x=.57	79.24±.97 S_x=.43	81.26±1.06 S_x=.47	85.15±.95 S_x=.42

To further test validity, an unbleached warp-face 1 × 2 cotton twill cloth, thread count 65 × 41, weight 4.53 oz./yd.² at 75° F. and 54% R.H., was substituted for Indian Head. A 4-factor (temperature, stroke, time, and detergent) experiment was run at 100° F. and 150° F. and at the same levels of the other factors as before. Again it showed all the main effects to be significant at the 99% level and in the same direction. No change in the order of ranking of washing machines or detergents resulted from change in cotton cloth. However, use of the twill cloth introduced more error than did the Indian Head.

It is sometimes desirable to explore interesting interactions by means of multilevel experiments [3]. Such experiments require a high degree of precision and reproducibility. Table II presents a multilevel experiment involving two factors. Factor A, detergent concentration, refers to a built anionic detergent, the main organic constituents being a mixture of alkyl aryl sulfonates and alkyl sulfates. Factor B, calcium ion concentration, refers to the addition of Ca^{++}, as chloride, to soft water and is reported in grains/gal. as $CaCO_3$. The conditions of the experiment are as follows:

Temperature: 150° F.	Load: 7 lb.
Agitator speed: 68 cycles/min.	Solution volume: 17 gal.
Time: 10 min.	Swatch: Indian Head

Seven levels of detergent concentration and six levels of calcium content are examined for per cent soil retention. The responses are plotted as Figures 6 and 7. In view of the strong interaction of detergent concentration and calcium content, the level of calcium content concentration must be specified when giving the effect of detergent concentration. For instance, soil retention is found to be relatively constant whether one washes with 0.1% detergent or 0.25% detergent at 0 grain hardness. However, the removal of soil is vastly improved if one washes with 0.25% detergent, instead of 0.1% detergent, at 16 grain hardness.

Conclusion

Zirconyl phosphate soil, precipitated in cotton fabric, answers requirements for evaluation and ranking of soil removal ability of washing machines and detergents. Validity of the zirconyl phosphate method is supported by experimental evidence that the independence of ranking is maintained over a wide range of particle size, type of cotton cloth, temperature, time, and water–load ratio. It is also supported by a framework of consistency with known or expected behavior of cotton cloth in washing machines.

Evidence of a high degree of reproducibility is the establishment of a consistent 48 block statistical design over a period of two weeks with reconstitution of the soiling solutions. The average standard error equal to 0.52% for washes of ten swatches (Table I-B) testifies to the precision of the method.

Measurement of ingrained soil removal is not obscured by redeposition and emulsification.

Acknowledgment

The authors wish to express their appreciation to Miss Beverly J. Brown, Mr. Robert Wheaton, and Mr. Donald C. Wood for the high quality of their experimental work and other contributions herein, and to other associates at Whirlpool Corporation for advice and interest in this work.

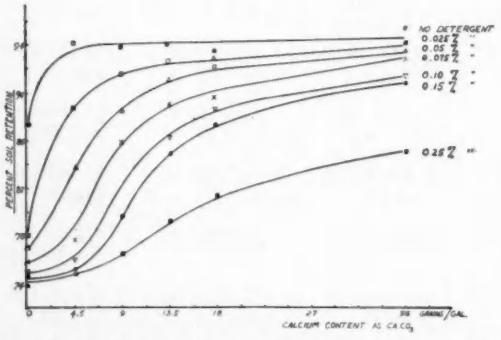

Fig. 6. Calcium content vs. % soil retention at various levels of detergent concentration.

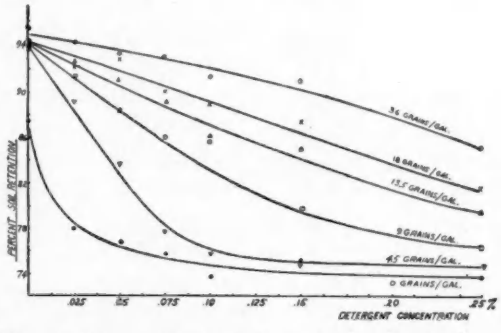

Fig. 7. Detergent concentration vs. % soil retention at various levels of calcium content.

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The Textile Institute Annual Conference—1958

The Textile Institute (Great Britain) will hold its Annual Conference May 12–16, 1958, in Edinburgh. The theme is to be "Fiber Blends and Mixtures."

Experimental Yarns from Partially Acetylated Cotton and Blends with Untreated Cotton

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Abstract

A number of experimental yarns were spun from partially acetylated (PA) cotton stock to determine some of the factors that improve its mechanical processing and yarn properties. These studies indicated that blending PA cotton stock with raw cotton was a better method of preparation for mechanical processing than the use of an antistatic treatment on the PA stock. Blending resulted in better mechanical processing and improved yarn properties at a lower cost. Blending high acetyl PA cotton with 40% raw cotton was considered to be the best method of preparation. PA stock prepared from a rain-grown cotton exhibited better mechanical processing characteristics than stock prepared from a longer-staple irrigated cotton. However, yarns spun from the latter type of PA cotton had better properties of strength, elongation, and flex abrasion resistance. The use of a higher twist multiplier in spinning and plying resulted in PA cotton yarns having improved properties of elongation and flex abrasion resistance.

Introduction

The first research on preparation and mechanical processing of partially acetylated (PA) cotton stock culminated in the development of satisfactory techniques for the acetylation of cotton raw stock in 30-lb. lots in a commercially available combination raw stock and package dyeing machine. The best products were spun into yarn through the use of selected antistatic agents. There were indications that even better processing and improved yarn products could be obtained using blends of PA and untreated cotton. These studies are described in a recent publication [5].

While the earlier yarns prepared from PA cotton stock were generally satisfactory, they had, for many uses, rather low elongation and flex abrasion endurance, and there were some processing difficulties experienced. In the work to be described, the objectives are to determine the relative merits of two widely different varieties of cotton for making PA cotton stock which can be satisfactorily spun into yarn, and to develop better and more commercially practical methods of handling PA cotton stock after acetylation. The latter should insure satisfactory mechanical processing and impart improved yarn properties, such as higher elongation and better flex abrasion endurance.

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Selection and Preparation of Stock

Description of Cottons

A commercial rain-grown cotton (Deltapine, $1\frac{1}{16}$-in. staple length) and a long staple finer variety of irrigated cotton (Mesilla El Paso, $1\frac{9}{32}$-in. staple length) were chosen for these studies. Deltapine (DPL) is a variety that is widely grown in the South and is considered to be a leading commercial cotton. Mesilla El Paso (MEP), grown in West Texas and New Mexico, is probably the longest staple irrigated cotton grown in this country, excluding the American-Egyptian varieties.

Methods of Preparation

PA cotton stock having an acetyl content of approximately 17–18% and 24–25% was prepared from each variety. Approximately 30 lb. of raw stock was acetylated in each lot.

The cotton stock was acetylated in a 50-lb. capacity combination raw stock and package dyeing machine using some modifications from earlier reported

procedures [2, 5]. The cotton was first presoaked over night in glacial acetic acid at 27° C. The acetylation mixture consisted of 75 parts glacial acetic acid, 25 parts acetic anhydride, and 0.15 parts perchloric acid. A temperature of 20° C. was maintained during acetylation. The time of acetylation for the different lots varied according to the variety of the cotton and the acetyl content, ranging from 45 min. to 1¼ hr. Following acetylation the stock was thoroughly rinsed with both cold and hot water until neutral to litmus. It was then centrifuged and dried.

PA cotton stock from each of the 30-lb acetylated lots was further prepared in two ways for mechanical processing: by treating with antistatic finishes and by blending with untreated cotton. A third portion was reserved, without further treatment, for processing through a card equipped with a radioactive type antistatic bar. A total of 22 five-pound lots were made up for study of processing characteristics. A diagrammatic schedule of these lots is given in Figure 1.

Blending with Untreated Cotton

The blended lots were planned to determine (1) the amount of untreated cotton needed in a blend with PA cotton stock to insure satisfactory processing and improved yarn properties, (2) the relative merits of blending PA cotton stock with untreated cotton of the same staple length or of using untreated cotton of a different staple length, and (3) whether PA cotton having a high acetyl content could be blended with larger amounts of untreated cotton and processed into yarns having properties equal to yarns spun from PA cotton of a lower acetyl content blended with less untreated cotton. The resultant acetyl content of the two blends should be the same, but the overall cost should be lower for the blend containing more untreated cotton.

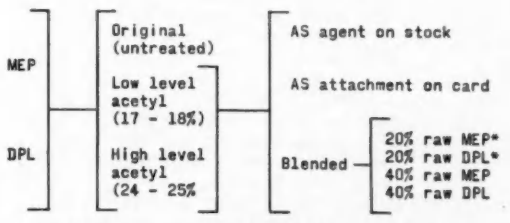

Fig. 1. Schedule of 5-lb. lots processed. A total of 20 PA lots and 2 untreated lots were processed.

The low acetyl PA cotton stocks were blended with 20% and 40% raw cotton of each variety. The high acetyl stocks were blended only with 40% raw cotton of each variety as previous processing experience has shown that a 20% blend with high acetyl stock could not be processed satisfactorily.

Effect of Yarn Twist on Properties

Each lot that processed well was made into 14/3 yarns using 3.5, 4.5, and 5.5 twist multipliers in spinning and plying to evaluate the effect of twist multiplier on yarn properties of strength, elongation, and flex abrasion. The effect of twist on the properties of yarns spun from PA cotton stock has not been previously determined.

Mechanical Processing

Processing Schedule

A list of processing machinery is given below, and with few exceptions, such as the fancy and a garnett wire feed roll on the card, the intention was to avoid special equipment and to conform to conventional processing procedures:

Opening.—The stock was fed by a hopper feeder into the SRRL opener [3, 4], then through a downstroke cleaner, and collected for manual feeding on the picker apron.

Picking.—The laps were made on a combination breaker-finisher picker with a pin beater speed of 900 rpm. The grid bars were adjusted to a one-half opening. Weight of finisher lap was 12 oz./yd.

Carding.—The card was clothed with #90 wire on the cylinder and #100 wire on the doffer and flats. It was equipped with a fancy and a feed roll covered with garnett wire. The sliver weight was 50 grains, delivered at 8 lb./hr.

Drawing.—A 4-roll drawing frame with synthetic cushion-top rolls was used with 6 ends up, producing 50 grain sliver—2 process drawing.

Roving.—From the drawing sliver a 1.50 hank roving was processed on a 10 × 5-in. long-draft intermediate roving frame.

Spinning.—The 14/1 yarn was spun single creel on a 3-in. ring, using twist multipliers of 3.5, 4.5, and 5.5.

Twisting.—The same twist multipliers were used in processing 14/3 yarns.

Characteristics Studied

The mechanical processing behavior of each lot was closely observed. The specific properties or processing characteristics studied in evaluating each lot are listed in Table I. A few of the more important of these were the amount of static present, appearance, uniformity, and ease of processing. Each PA lot was given an overall evaluation of satisfactory, fair, or unsatisfactory. Those lots described as satisfactory processed without any difficulty, though not necessarily as well as untreated cotton. Those described as fair processed without any serious difficulties, but the appearance, uniformity, and overall processing quality were not as good as the satisfactory lots. The card webs of these lots exhibited more neps and had a harsher feel. There was more fiber friction or drag, and in some cases slight loading of the card cylinder resulted. The lots which were unsatisfactory exhibited excessive static upon carding and, with one exception, could not be carded and collected into sliver.

Classification of Lots

The lots of PA cotton evaluated as satisfactory and fair, on the basis of their mechanical processing, are shown in Table II. All of the PA lots classed as satisfactory were prepared from Deltapine cotton. Comparable PA lots prepared from Mesilla El Paso cotton were described as fair. Three PA lots prepared from Deltapine cotton were in the fair category. Only one of the comparable MEP lots was in this category, the other two being unsatisfactory (not shown in table). It is apparent from these data that the Deltapine PA cotton stock processed better than the Mesilla El Paso PA cotton stock.

A total of 5 PA cotton lots were considered satisfactory, 9 lots were fair, and 6 were unsatisfactory. The latter included the 4 lots of PA cotton that were processed on a card equipped with antistatic bars, the blend of Mesilla El Paso PA cotton with 20% Deltapine raw cotton, and the blend of Mesilla El Paso cotton with 20% Mesilla El Paso raw cotton. Although its processing was considered unsatisfactory, the latter blend was processed into yarn and the test data are reported.

All but one of the satisfactory lots were blends of 40% untreated cotton with the acetylated stock. The lone exception in the satisfactory group, the better-running Deltapine PA cotton with the lower degree of acetylation, treated with the preferred antistatic agent, does not seem misplaced. As might have been expected, all of the 40% blends processed better than comparable 20% blends. There is no clearcut indication of superiority between the 40% blended lots and the antistatic treated lots, insofar as processability is concerned. As will be shown, however, the blended lots gave yarns superior in many other respects.

The processing results did not indicate any particular advantage or disadvantage in using untreated cotton of the same or different staple length for blending. This is illustrated by comparable blended lots being in the same category.

Another conclusion reached is that PA cotton stock having a high acetyl content can be blended with 40% untreated cotton and processed better than PA cotton stock having a lower acetyl content blended with 20% untreated cotton. While both blends have approximately the same acetyl content and produce yarns with similar properties, including

TABLE I. Mechanical Processing Evaluation Characteristics

Carding:
1. Static
2. Loading
3. Speed
4. Appearance
5. Neppiness
6. Fiber separation
7. Feel

Drawing:
1. Appearance of web
2. Drafting uniformity
3. Fiber separation
4. Appearance of sliver

Roving:
1. Uniformity
2. Running performance
3. Ends down

Spinning:
1. Ends down

TABLE II. Mechanical Processing of PA Cotton Stock
(Acetyl content shown in parenthesis)

Satisfactory:

DPL (18%) with AS agent
DPL (18%) with 40% raw DPL
DPL (18%) with 40% raw MEP
DPL (25%) with 40% raw DPL
DPL (25%) with 40% raw MEP

Fair:

DPL (18%) with 20% raw DPL
DPL (18%) with 20% raw MEP
DPL (25%) with AS agent
MEP (17%) with AS agent
MEP (17%) with 40% raw DPL
MEP (17%) with 40% raw MEP
MEP (24%) with AS agent
MEP (24%) with 40% raw DPL
MEP (24%) with 40% raw MEP

heat resistance, there is a definite cost advantage in favor of the high acetyl–40% blend.

The size of the lots was limited to 5 lb. because of the large number of comparisons that were made. It was felt that 5-lb. lots were adequate to furnish the necessary data to make these comparisons. No attempts were made to determine the optimum machine settings and processing schedule for running PA cotton; this would require larger lots. Because PA cotton has different physical properties [5] and processing characteristics as compared to raw cotton, the same machine settings and processing sequences used for raw cotton are not necessarily those that are best for PA cotton. It is believed that the processing characteristics of PA cotton can be even further improved when the optimum machine settings and processing sequences are determined.

Tests on Yarns

Yarns were tested for single strand breaking strength [1a], elongation at break, and flex abrasion resistance [1b]. Breaking strength is expressed as count-strength product so as to equalize small variations in yarn count. Count-strength products were also determined on the PA cotton yarns, after heating 7 da. at 160° C. in a laboratory oven, to determine to what extent blending affected the heat endurance properties.

Comparison of Yarn Properties

MEP versus DPL

The properties of PA cotton yarns from MEP and DPL stock, prepared in 5 different ways for mechanical processing, are compared in Figure 2 on the basis of count-strength product, elongation at break, and flex abrasion endurance. These data show very clearly that the Mesilla El Paso PA cotton yarns were superior in almost every comparison. This is doubtlessly due, at least in part, to the superiority of MEP cotton before the treatment. This intuitive concept is, therefore, confirmed by these experiments.

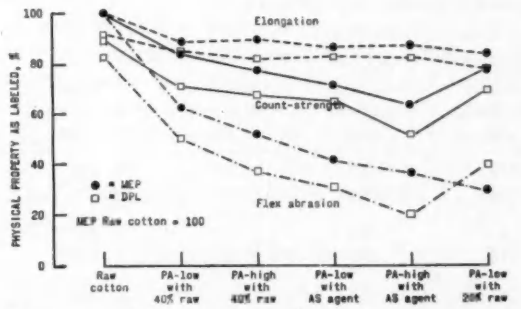

Fig. 2. Properties of MEP and DPL PA yarns. The order of plotting along the horizontal axis is arbitrary.

Blends versus Antistatic Treatment

A comparison of the properties of MEP and DPL partially acetylated cotton yarns, prepared by treating low acetyl PA stock with an antistatic finish and by blending with 20% and 40% raw cotton, is given in Figure 3. The data indicate that yarns spun from blends of PA cotton stock with 40% raw cotton had slightly more elongation at break, higher count-strength products, and much better flex abrasion resistance than the PA yarns having an antistatic finish or those blended with 20% raw cotton. The yarns prepared from blends of PA cotton with 20% raw cotton and from PA cotton having an antistatic finish were similar in most properties. The elongations of the six PA cotton yarns averaged about 89% of that of the yarns from raw cotton. Count-strength products of the PA cotton yarns varied from 72–84% of the untreated, which is largely accounted for by the gain in weight upon acetylation [5]. Flex abrasion resistance of the PA cotton yarns was low, averaging only 47% of that of the yarns from the untreated cottons. However, the flex abrasion resistance of the yarns prepared from PA cotton blended with 40% raw cotton was about 50% better than that of the other PA cotton

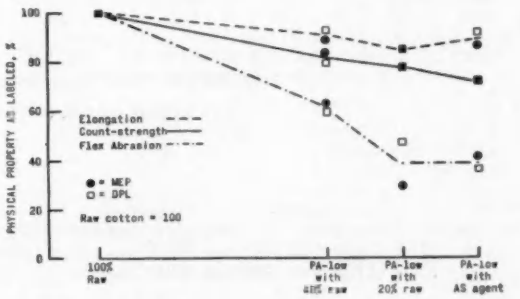

Fig. 3. Properties of antistatic treated and blended lots prepared from PA cotton of 17–18% acetyl content. The order and spacing of points along the horizontal axis are proportional to content of PA cotton in the blend. (Black squares represent coincidence of white squares and black circles.)

yarns and averaged 62% of that of the untreated yarns.

Yarns spun from high acetyl PA stock blended with 40% raw cotton had higher count-strength products and better flex abrasion endurance than high acetyl PA yarns having an antistatic finish (Figure 2). There was little difference in the elongation at break in these comparisons.

MEP versus DPL Raw Cottons in Blends

Yarns were prepared from blends of four PA cotton stocks (MEP of 17 and 24% acetyl and DPL of 18 and 25% acetyl) with 40% raw MEP and with 40% raw DPL cotton. The data in Table III show that the yarns prepared from blends of PA cotton with MEP raw cotton were superior in strength, elongation, and flex abrasion endurance.

Different Blends Having the Same Actyl Content

The data in Table IV give the properties of yarns spun from two types of blends, both of which had approximately the same calculated acetyl content after blending. A blend of MEP low acetyl PA cotton stock and 20% raw MEP was compared with a blend of MEP high acetyl PA cotton stock and 40% raw MEP. In a like manner blends of DPL low and high acetyl PA stocks with 20% and 40% raw DPL were compared. DPL PA cotton stocks blended with 20% and 40% raw MEP were also compared. In most of these comparisons the yarn properties were approximately the same. It has been shown that high acetyl PA cotton blended with 40% raw cotton processed better than low acetyl stock blended with 20% raw cotton. Since the yarn properties are equally as good, and since the cost of making PA cotton yarn by this method is less, it appears to be the better method of blending.

Effect of Twist Multiplier Upon Yarn Properties

On Strength

PA cotton yarns were prepared using 3.5, 4.5, and 5.5 twist multipliers in spinning and plying.

TABLE III. Effect of Different Raw Cottons in 40% Blends

(Acetyl content of PA stock shown in parenthesis)

	Raw cotton component					
	MEP			DPL		
PA cotton component	Count-strength product, lb.	Elongation at break, %	Flex abrasion, cycles	Count-strength product, lb.	Elongation at break, %	Flex abrasion, cycles
MEP (17%)	22.1	13.3	392	19.8	12.2	333
MEP (24%)	20.8	13.5	324	19.0	13.7	280
DPL (18%)	19.4	13.1	381	18.9	12.7	312
DPL (25%)	18.9	13.8	294	18.0	12.3	232

TABLE IV. Yarn Properties of Blends at Constant Acetyl Content

(Acetyl content of PA stock shown in parenthesis)

Description	Acetyl content* of blend, %	Count-strength product, lb.	Elongation at break, %	Flex abrasion, cycles
MEP (17%) with 20% raw MEP	14	20.7	12.7	185
MEP (24%) with 40% raw MEP	14	20.8	13.5	324
DPL (18%) with 20% raw DPL	14	18.5	11.7	250
DPL (25%) with 40% raw DPL	15	18.0	12.3	232
DPL (18%) with 20% raw MEP	14	19.7	12.2	285
DPL (25%) with 40% raw MEP	15	18.9	13.8	294

* Calculated.

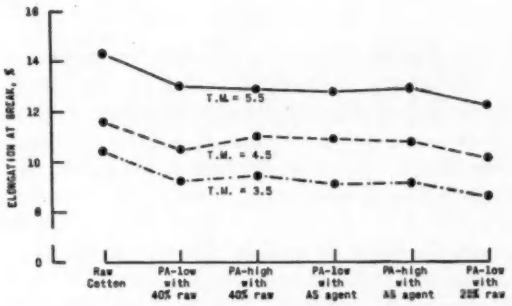

Fig. 4. Effect of twist multiplier on elongation of PA cotton yarns. The order of plotting along the horizontal axis is arbitrary. Data shown represent the average of MEP and DPL values.

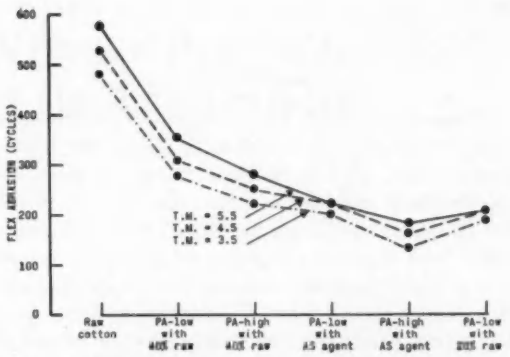

Fig. 5. Effect of twist multiplier on flex abrasion of PA cotton yarns. The order of plotting along the horizontal axis is arbitrary. Data represent the average of MEP and DPL values.

PA cotton yarns spun using a 4.5 twist multiplier averaged about 5% stronger than those spun using a 3.5 or 5.5 twist multiplier. This observation, while statistically significant, does not outweigh other more outstanding advantages of using a higher twist multiplier which are described in the following paragraphs.

On Elongation at Break

Variations in twist multiplier had a pronounced effect on the elongation at break of all the yarns prepared (Figure 4). The PA cotton yarns spun using a 5.5 twist multiplier had elongations at break averaging 40% higher than those spun using a 3.5 twist multiplier, while those spun using a 4.5 twist multiplier were intermediate (elongations 17% greater). The same trend was apparent with the yarns spun from the untreated cottons.

On Flex Abrasion Resistance

The flex abrasion resistance of all the PA cotton yarns was greatest when a higher twist multiplier was used in spinning and plying. Yarns spun using a 5.5 twist multiplier averaged 23% better flex abrasion resistance than those spun using a 3.5 twist multiplier while those spun with a 4.5 twist multiplier were 13% better in this respect. A similar trend was noted for the yarns prepared from untreated cotton. Data are plotted in Figure 5.

Heat Endurance of PA Cotton Yarns

The relative strengths before and after heating are given in Table V for PA cotton yarns prepared from blends of high acetyl PA cotton stock with 40% raw cotton and PA cotton yarns prepared from low acetyl PA cotton stock having an antistatic finish. The data show that yarns prepared from blends of high acetyl PA cotton with 40% raw cotton averaged 6% stronger before heating and about 9.5% stronger after heating than comparable yarns prepared from low acetyl unblended PA cotton stock having an antistatic finish. The relative strengths after heating indicate that the more heat-resistant high acetyl PA cotton stock can be blended with 40% raw cotton and still produce yarns having equal or better heat resistance than yarns produced from low acetyl PA cotton stock having an antistatic finish. Although untreated cotton produces stronger yarn than PA cotton, the strength before heating of the high acetyl blended PA yarns is not much greater than that of the low acetyl antistatic treated PA yarns because high acetyl PA cotton stock does not

TABLE V. Comparison of Heat Endurance of PA Yarns
(Blends versus antistatic-treated)

	Relative strengths* before heating, %	Relative strengths* after heating,** %
MEP (17%) with AS agent	100	100
MEP (24%) with 40% raw MEP	109	106
MEP (24%) with 40% raw DPL	100	115
DPL (18%) with AS agent	100	100
DPL (25%) with 40% raw DPL	105	113
DPL (25%) with 40% raw MEP	110	104

* Low acetyl antistatic-treated yarn in each comparison = 100.

** Heated 7 days at 160° C.

produce yarn as strong as low acetyl PA cotton stock (Figure 2).

Summary

These studies have led to several general conclusions. Deltapine PA cotton is preferable to the longer staple Mesilla El Paso PA cotton from the standpoint of mechanical processing characteristics, but the yarns spun from Mesilla El Paso PA cotton stock have superior properties of strength, elongation at break, and flex abrasion resistance. The use of a higher twist multiplier in spinning and plying PA yarns prepared from both varieties of cotton resulted in yarns having higher elongation and better flex abrasion endurance. Perhaps the most important conclusion is that from the standpoints of mechanical processing, yarn properties, and cost, the blending of high acetyl PA cotton stock with 40% raw cotton is the best method of preparing PA cotton stock for mechanical processing.

The data obtained in these studies will be used in the preparation of PA cotton fabrics from PA cotton stock for comparison with fabrics acetylated in the fabric form. It is believed that better fabric properties, such as improved tear strength and flex abrasion resistance, can be obtained by preparing fabrics from PA cotton stock blended with raw cotton.

Acknowledgments

The authors' thanks are due to many members of the staff of the Southern Regional Research Laboratory who have cooperated in these studies. Processing experiments were conducted by A. T. Callegan, J. J. Brown, and other members of the Cotton Mechanical Processing Section. Raw stocks were acetylated by A. L. Murphy and M. J. Hoffman of the Cotton Chemical Processing Section. Drawings of figures were prepared by N. A. Cashen. The physical testing was performed by A. R. Markezich, J. P. Evans, and W. F. McSherry of the Textile Testing Unit of the Analytical, Physical-Chemical, and Physics Section.

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Direct Dye Staining of Viscose Rayon Cross Sections and Some of Its Applications

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Abstract

A differential staining method for the skin of viscose rayons is described. The procedure consists in the dyeing of fiber cross sections by a blue direct dye, Azine Brilliant Blue, followed by washing through the usual alcohol series. Being so simple in operation and involving no special technique, it can be used conveniently for routine work. The results obtained are identical to those of the Victoria Blue method and are comparable to results using the Gentian Violet method.

It is most probable that all these microscopical stains differentiate between the skin and core in the normal viscose rayons only in terms of physical phenomena, such as diffusion, absorption, and swelling. The skin is stained much more slowly, but retains the dye much more strongly than the core, which is quickly dyed and readily washed out.

The present technique has been applied to a wider range of cellulosic fibers. Among others, cotton and BX fiber (a French viscose rayon produced by high concentration sulfuric acid spinning) are shown to be similar to the core, while mercerized cotton, Shintoramomen (a Japanese viscose rayon staple produced by low concentration sulfuric acid spinning), and Fortisan (a rayon regenerated from cellulose acetate) are found to be like the skin in their respective staining properties.

Introduction

Since the skin effect in viscose rayons was first demonstrated by Preston [11], Ohara [10], Schramek [13], and others, a number of techniques for the selective staining of the skin and core have been described. Among them the most interesting and notable is the Victoria Blue skin staining disclosed by Morehead and Sisson [9] and modified by Hermans [4], which makes possible a sharp differentiation between the skin and core. More recently a new method was developed by Berry [1], in which Gentian Violet in combined use with a direct dye stains the skin a deep purple color. However, either of these basic dye procedures involves a washing step too highly critical to be adapted for routine use.

In Japan, on the other hand, the Oxamine Blue method, in which the dye stains the skin a pinkish tint and the core a deep blue, has been widely used [3, 6, 7], according to Ohara's original work [10]. This differential coloring effect, however, is not necessarily so sharp for every type of viscose rayon, but rather eventually makes obscure the contrast between the skin and core in photomicrographs taken.

The present investigation is concerned with staining the skin area selectively by using direct dyes, which have been found to give results identical to those of the Victoria Blue method cited above.

Experimental Procedure

Slide Preparations

Cross sections about 5 μ thick are required. The standard paraffin embedding can be used; microtome sections are fixed on the slide by the usual albumin adhesive. The preembedding of fiber specimens in agar agar gels as described by Horio et al. [6] is recommended in order to obtain preparations of better quality. The addition of PVA to agar agar (in the ratio 1:5) recently has been found by the author to be effective in allowing even the highest tenacity rayons to be sectioned much more easily. Naturally, before the staining procedure the agar agar-PVA should be removed from preparations by boiling in water.

Staining Solution

Several blue direct dyes can be used, among which Azine Brilliant Blue (C.I. No. 512 or No. 518) was found to be most suitable. According to the sub-

sequent survey Sirius Supra Blue B (Bayer) also has proved to be preferable for the purpose concerned.

However, because every lot of the same dye does not necessarily give equally good results, it is essential to select empirically the best lot, which must not leave any tint in the core portion after the washing step through alcohol. Any dyes showing a reddish spot in the front of the blue main spot of a simple paper chromatograph were abandoned.

The staining solution is prepared by dissolving 1% dye and 10% sodium chloride in distilled water. This solution can be used repeatedly for 2–3 months.

Staining Procedure

The slide preparations are heated in a beaker containing the above solution on a water bath, being kept at the boil for about 30 min., then are freed of excess dye by dipping in a beaker of water, immediately followed by the dehydration step through the usual alcohol series. The dye absorbed by the fiber cross sections bleeds off from the central core largely in dilute alcohol (50 to 80%); 90% and above shows no washing action.

This differentiating process through the alcohol series is not so critical as is the case in the Victoria Blue method, using dioxane or ethyl alcohol, and the Gentian Violet method, using denatured alcohol. The skin is so different from the core in the retaining force against direct dyes that the differentiation proceeds in a steady manner and results in a consistent staining of the skin layer without any particular skill applied.

After dehydrating and clearing, the preparations are mounted by Canada balsam in permanent form;

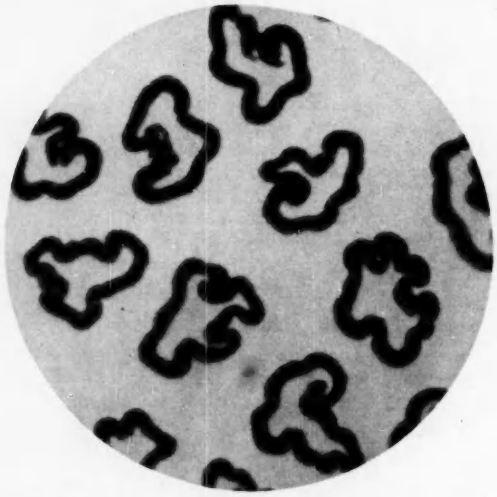

Fig. 1. A conventional tire cord rayon showing a typical skin-core effect (758 ×). (Unless otherwise stated, cross section preparations are stained with Azine Brilliant Blue, mounted in Canada balsam, and photographed with an orange yellow filter.)

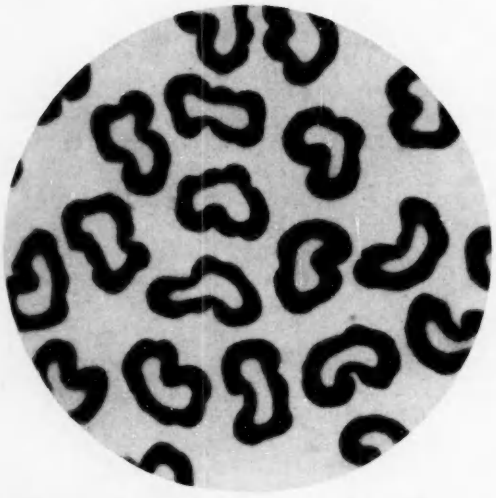

Fig. 2. A super cord rayon showing fairly thick skin (758 ×).

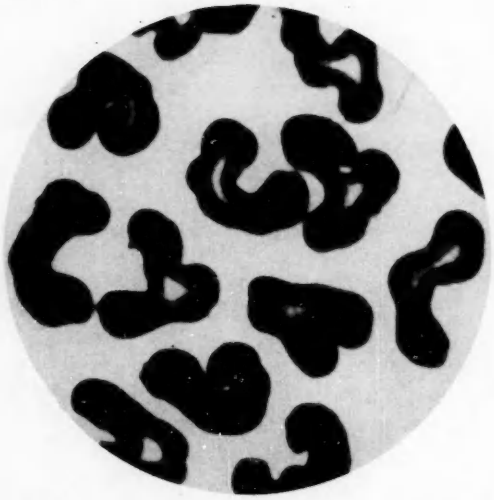

Fig. 3. Another super cord rayon showing extremely thick skin (758 ×).

on mounting in glycerine the dye disappears gradually from the cross sections.

Results and Discussion

The typical skin-core effect can be observed particularly in tire cord rayons. By means of the procedure described above the skin is selectively stained in deep blue while the core remains undyed. By way of example, a conventional and two super types are shown in Figures 1–3 in order of increasing thickness of the skin. Orange yellow filters are always used for photomicrographing in black and white.

Canada balsam employed as permanent mountant has a refractive index nearly equal to that of viscose rayons, so that the mounted sections would be dissolved optically if the dyed skin layer is not present. Thus, in Figure 4 an irregular distribution of the skin around each filament is clearly demonstrated in a sample of harsh yarn. On the other hand, another mountant, *e.g.*, glycerine, is sometimes effectively used as shown in Figure 5, where the hollows within the core of a special type rayon become visible only because of the optical effect involved.

Although the differential staining of the skin and core in viscose rayons was explained by earlier workers on the basis of a higher degree of orientation in the skin, subsequent investigators [1, 4, 6, 9] have shown it most probable that only physical phenomena, such as diffusion and absorption of the dyes and swelling of cellulose gels, are concerned herein. Consequently, whether basic dye such as Victoria Blue [4, 9] and Gentian Violet [1], or direct dye such as Congo Red [11], Oxamine Blue [10], and others are used, the staining processes in each case are observed to proceed basically in a similar manner. In the early stage only the core is dyed, the skin remaining undyed except for the outermost thin layer, as shown in Figure 6. Such a core staining also is

Fig. 5. A special type rayon mounted in glycerine, showing many hollows within the core (758 ×).

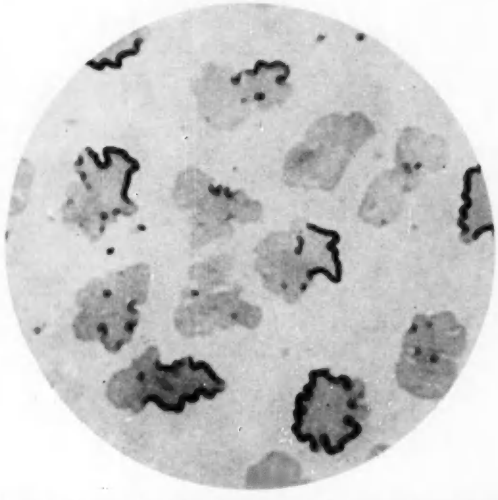

Fig. 4. A sample of harsh yarn showing an irregular skin distribution (379 ×).

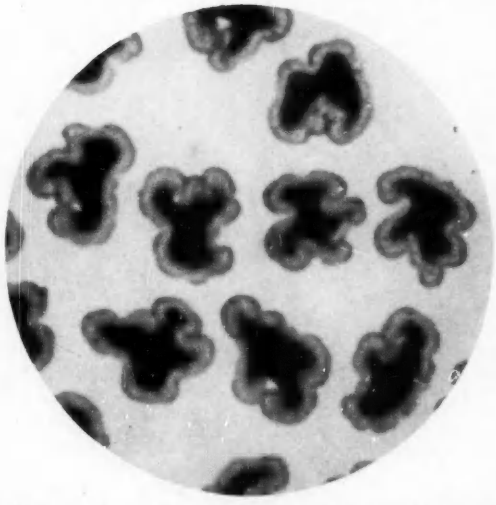

Fig. 6. Early stage of staining in the same specimen as shown in Figure 1, indicating the core deeply stained (758 ×).

of significance in supplying information on the character of the core produced under various conditions.

As the staining proceeds, eventually the entire cross section is deeply dyed, indicating no difference present between the skin and core. Only in the subsequent washing process comes a differentiation, resulting in the selective skin staining. It is well known that the basic dye methods involve a washing step so extremely critical that washing solutions and/or washing time should be under a strict control and check.

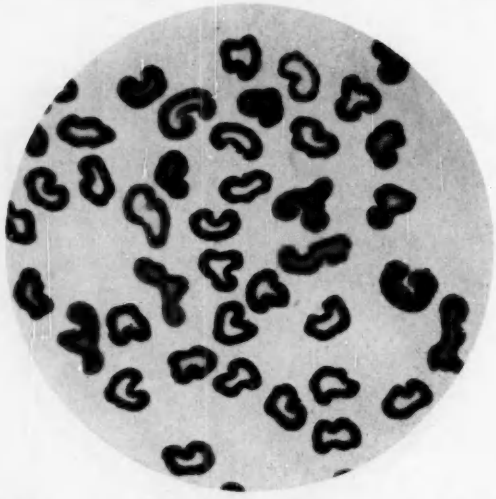

Fig. 7. Silver staining on the same two super cord rayons as shown in Figures 2 and 3, indicating the skins stained in different degrees (379 ×).

Since the earliest investigations on this subject much use has been made of direct dyes. Among them Sky Blue FF (C.I. No. 518) was used preferentially by Preston and his coworkers [8, 12], who carried out the washing with pyridine water and obtained results corresponding to the data presented here.

Because of the slower rate of dyeing with direct dyes compared with basic dyes, it has been necessary to stain slide preparations under such severe conditions as adopted in the present procedure. However, the advantage is that the following essential step, the differentiation, requires no particular consideration and skill. As described above, an ordinary passing through the usual alcohol series results in consistently excellent differential staining of the skin.

In our laboratory the present staining technique has not only been employed for routine use, but also applied to a wider range of cellulosic fibers, both native and regenerated. Obviously, in order to gain correct understanding, it is imperative to use a variety of staining procedures simultaneously and to compare the results. It should be mentioned here that the silver staining introduced by E. C. Jolliff [5] furnishes very interesting results, although its staining mechanism is not yet explained. In fact,

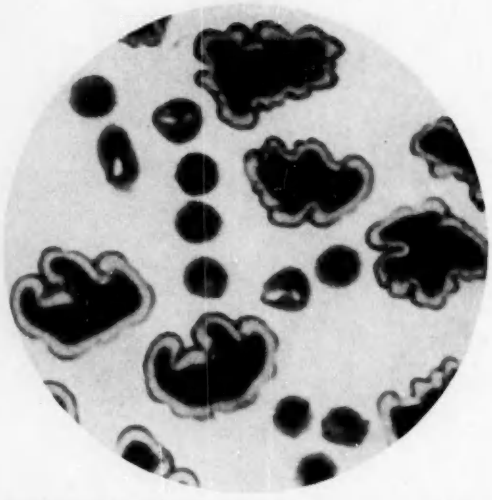

Fig. 8. BX fiber together with a tire cord rayon as control shown in the stage of the core staining (758 ×).

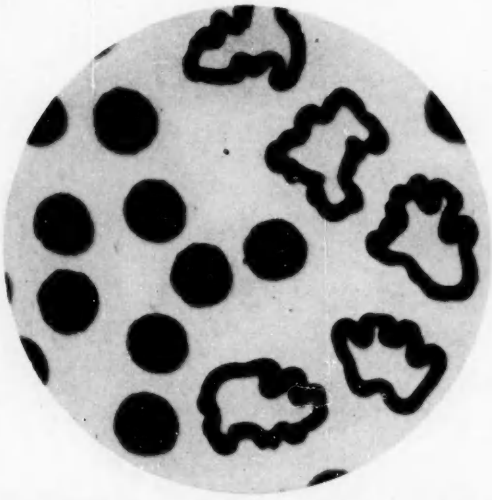

Fig. 9. Shintoramomen together with a tire cord rayon as control, shown in the stage of skin staining (758 ×).

this procedure frequently enables one to detect a slight, otherwise indistinguishable difference in the skin consistency, as shown in Figure 7.

As a result of this work it is realized that microscopical study employing staining techniques is still one of the most fruitful approaches to the elucidation on the fine structure of cellulose fibers. Therefore, it is believed that they should find more increasing use combined with the electron microscopical methods.

In this paper only a few conclusions drawn on the basis of optical microscopic observations are described.

BX fiber [2] is found to be core-like in comparison with a conventional tire cord rayon, while Shintoramomen [14, 15] is shown to be skin-like (Figures 8 and 9).

On the other hand, cuprammonium rayon shows no skin proper, but its central portion is rather closer to the skin than the distinct outer layer in their respective staining behaviors (Figure 10). Similarly it has been found that Fortisan may be termed an all-skin type rayon, though it is stained with much more difficulty than Shintoramomen.

Native cotton fiber can be compared to the core in contrast with mercerized cotton, which has been demonstrated to become skin-like in the treatment involved (Figure 11).

There is shown another example in Figure 12, where due to the impregnation with resin the core in a sample of rayon staple has changed its staining property to that of the skin. This observation might fairly well indicate that the difference between the skin and core lies solely in the fineness of cellulose gel networks.

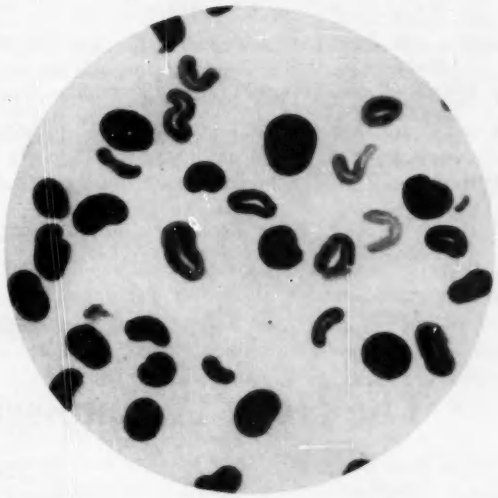

Fig. 11. Cotton fibers before and after mercerization, prepared with Gentian Violet method, showing mercerized rounded fibers deeply stained and untreated flat shaped fibers slightly stained (379 ×).

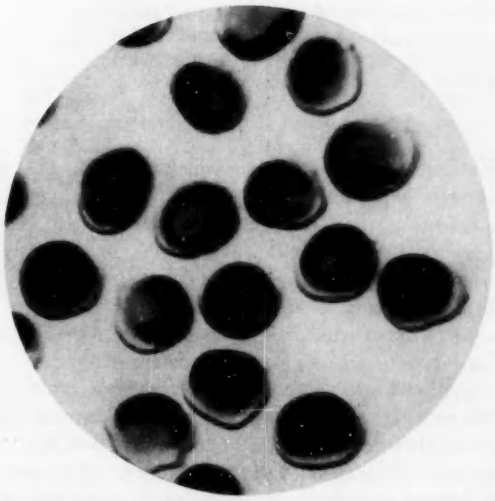

Fig. 10. Cuprammonium rayon mounted in glycerine, showing the central portion stained after relatively short washing (758 ×).

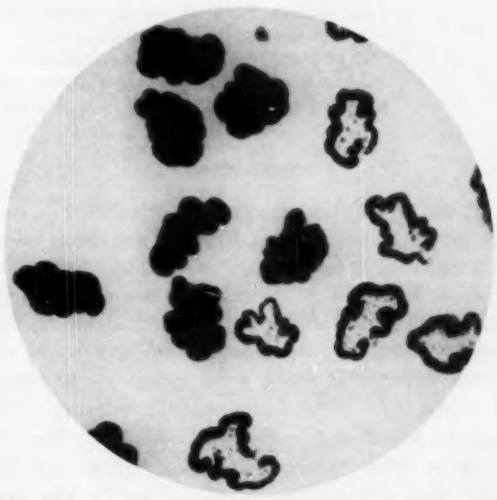

Fig. 12. Effect of resin finishing on a rayon staple, the core having changed its staining property due to the resin impregnation (379 ×).

Acknowledgments

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The Heat Transmission of Fabrics in Wind

C. D. Niven

Abstract

Two samples of overcoating material were tested for heat transmission in wind when an air space under the material was provided. The effect of a wind breaker both under and over the material was observed. The work shows that when a sample has a high permeability to air and does not lie close to the hot plate, there is a very marked difference between the results obtained with a wind blowing parallel to the surface and those with the wind striking the surface at 45°. The work also proves that the thermal insulation afforded by a fabric or combination of fabrics in wind depends on what is underneath the sample and suggests that some purely arbitrary test procedure, specified by a standardizing authority, may be desirable.

Introduction

At the present time no standard procedure of test has been specified for assessing the insulation value of a garment in wind; little, in fact, has been published in the technical journals on this subject. In 1934 Black and Matthew [1] published some results on wool and linen; the measurements were made on a katathermometer using wind speeds up to about 12 m.p.h. In 1943 Schiefer [8], working with blankets and sheets, made some hot plate measurements in wind "when a stream of air moving 15 m.p.h. was directed across the sample." The hot plate, as developed by Cleveland [2] for this work, is a good standardizing method, but as the work described below will show, Schiefer's work did not take into consideration certain difficulties inherent in assessing insulation value in winds. In 1946 Pierce & Rees [7] published results on extensive research on the transmission of heat through textile fabrics, but only a little information was reported on the effect of wind; the method used for the measurements in wind was a rate of cooling method.

During World War II the problem was one of military significance; investigations were carried out by Day [3] for the Quartermaster Corps Climatic Research Laboratory, Lawrence, Mass. This valuable work was, however, described in restricted reports; although these are now declassified, the information never reached the technical journals. Day

used the cylinder method, essentially similar to the method which Dr. J. D. Babbitt [5] and the writer had used for measuring the insulation value of indoor clothing, except that Dr. Day did not use heated end guards. Larose [4], who also worked on the insulation problem during the war, discarded the cylinder method in favor of the hot plate method.

The hot plate used in the present investigation is the actual hot plate which Dr. Larose used for his work; the cylinder used in the present work is of more recent construction. The writer had this constructed because there was some uncertainty as to whether the hot plate and the cylinder results would agree. When the sample lies close to the metal in still air, results agree satisfactorily, but this agreement was only achieved after the greatest care had been used to prevent end heat losses. Furthermore, when the sample lies close to the metal, even in winds, the writer found very little difference between the measurements made on the hot plate in winds approaching the plate at 0° or 45° and the measurements on the cylinder.

These results did not appear to the writer to be wholly satisfactory because they disagreed with what one intuitively expected. The obvious suggestion was that, while the apparatus was giving the true answer, the conditions of test might not be simulating everyday wearing conditions sufficiently well. The work described below was undertaken accordingly, in order to ascertain how an airspace under the overcoatings which had previously been tested would change the results. As soon as this was done, quite a pronounced difference showed up between tests in the 45° and 0° winds on the hot plate. The results were so encouraging that it seemed worthwhile to see how the test method would show up the beneficial effect of a wind breaker.

It must be emphasized that the investigation was directed mainly to finding out something about conditions of testing, rather than to getting information on the particular samples and combinations.

Methods

The apparatus used for measuring the thermal conductance was essentially the same as that used for the previous tests [6], when the sample was tested close to the plate or cylinder surface. The hot plate for these tests was designed so that it could be tilted to permit the making of measurements in winds approaching the surface at 0° or 45°. For brevity these tests will be referred to below as the "0° plate test" and the "45° plate test." For the cylinder tests, the smaller of the two ducts used in the previous work was used throughout the present investigation.

In order to simulate a loose garment for the cylinder test, the material was sewn over two rings R at either end of the heated cylinder as shown in Figure 1a. The rings were formed by winding rubber tape until a thickness of about $\frac{1}{2}$ in. was built up. It was found that since cloth has a certain amount of expansion, it was hard to get the cloth tight on the rings without "drawing in" where it was not supported by the rubber. When, on the other hand, the sample was sewn on in such a way that it was about $\frac{1}{2}$ in. from the surface of the cylinder all along the length, it was loose at the ends. To prevent air from blowing in beneath the sample under these conditions, a piece of copper wire W was wound around and fastened tightly. To test the effect of a wind breaker on the outside of the sample, a piece of vinylite sheeting was wrapped around and sealed with a strip of cellophane tape.

In the case of the plate a grid was used to hold the sample away from the metal surface; it consisted of a piece of $\frac{1}{2}$ in. mesh wire screening mounted on a frame of $1\frac{1}{2} \times \frac{3}{8}$ in. wooden slats and soldered

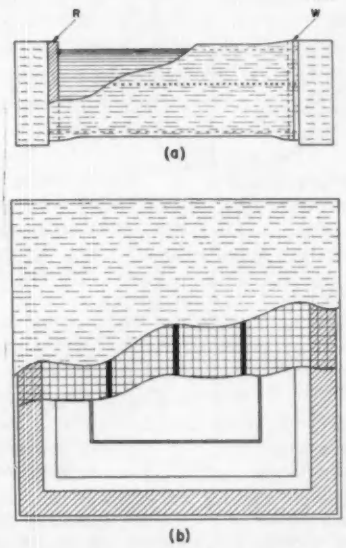

Fig. 1. (*a*) Diagrammatic illustration of sample on heated cylinder. (*b*) Diagrammatic illustration of sample on hot plate.

to three $\frac{1}{4}$ in. square brass rod stiffeners to prevent sagging and touching the plate. The arrangement is shown in Figure 1b. The samples of cloth were tacked to the grid in five places—at the center of the plate and at the center of each quarter. The vinylite wind breaker, when on top of the sample, was not tacked down. In high 0° winds it rose considerably; three weights were employed to hold it down. As the test without a wind breaker shows that the 0° plate method is not satisfactory, the small error introduced by the weights is not important. For the 45° plate test the sheeting was allowed to take its natural position.

After the work had been completed using the above techniques, a special device was constructed for clamping the sample on the hot plate in an attempt to keep air from leaking in under the sample during test. This device consisted of two squares of angle iron fitting inside each other and clamped together at each of the corners by means of a bar with screws and wing nuts. The measurements on the 45° hot plate were repeated at approximately 16 m.p.h. and in still air, using this device and tacking all samples or combinations of samples to the grid in five places. As will be shown in the discussion of results below, the effect of these elaborations was slight and unimportant. The clamping device could be used only for the 45° tests; for the 0° plate tests it caused a decrease in the clo value. This was evidently due to the clamp causing turbulence in the air stream, because when the upper half of the clamp was removed, the decrease in clo value was less pronounced. The clamp was in fact introducing another kind of error, which was more objectionable than the possibility of a small air leak. Owing to the fact that measurements could not be made on the 0° plate when the clamp was used, only measurements on the 45° plate with and without the clamp have been reported below for comparison purposes.

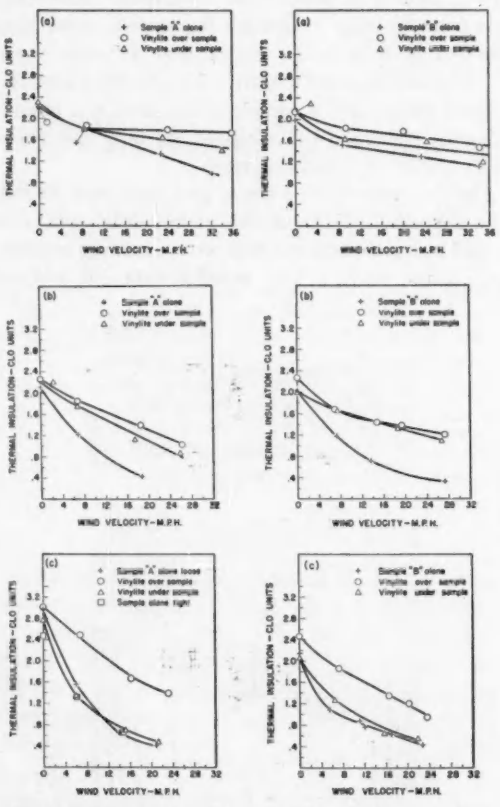

Fig. 2. Curves showing the effect of wind velocity on the thermal insulation of overcoating samples A and B with and without vinylite wind breaker, (*a*) on hot plate with wind striking plate at 0°, (*b*) on hot plate with wind striking plate at 45°, (*c*) on heated 5 in. cylinder. (Tests were conducted under special conditions described in the text and illustrated in Figure 1.)

Results and Discussion

The results are shown in the graphs. Since each sample was tested in three apparatus arrangements (1) alone, (2) with the windbreaker over the sample, and (3) with the windbreaker under the sample, the results for each sample can be grouped in three sets of three graphs; these are marked (a), (b), and (c). Graph (a) indicates that the results were obtained on the 0° plate, (b) on the 45° plate, and (c) on the cylinder. Sample A was 0.173 in. thick; it had an air permeability of 52 cu. ft./sq. ft./min., and its thermal insulation in clo units in still air was 0.83. Sample B was 0.127 in. thick, had an air permeability of 37 cu. ft./sq. ft./min., and an insulation value of 0.63.

The graphs relating to the 0° plate tests indicate that no very large advantage would be expected from wearing a windproof garment, and as this is contrary to the experience of countless people who use windbreakers, it is safe to conclude that this method of testing should be ruled out as quite unsatisfactory. In sharp contrast, the 45° plate tests show that for both the overcoating materials, the insulation is much greater when a wind breaker is used, regardless of whether the windbreaker is on the inside or on the outside. Figure 3, which refers to the 45° plate test

using the special clamping device, confirms this conclusion. It is of interest to point out that in still air there was no marked difference between the 45° and the 0° plate measurements, thus proving that convection currents in the air space when the plate was tilted were not interfering with the results. Since the stiffeners on the grid lay across the tilted plate, they helped to stop any movement of air up and down the inclined plane; in any case a verticle hot plate gives the most trouble in testing when large air spaces are present.

The graphs relating to the cylinder tests show that the wind breaker was very effective on the outside, but was almost useless on the inside. Apparently the wind must have blown the vinylite against the metal cylinder on the 'up wind' side; since the plastic has negligible insulation, it must have given no protection on the very side of the heated body on which it was needed. The cylinder tests on the A sample were conducted with the cloth sewn on much more loosely than in the case of the B sample. The A sample was subsequently tested under tighter conditions, with the material drawn in as shown in Figure 1a, where it was not supported by the rubber rings. The graphs show that the effect of looseness was not really important; this is to be expected because the thickness of the air space would be important only when it was so small that air movement in the air space would be severely hindered.

Figure 3 shows that the results on samples A and B are almost identical, suggesting that a relatively less permeable wool fabric is not effective in stopping heat loss in wind, at any rate when there is an air space underneath. Under wearing conditions, lining, padding, and other clothing might modify this laboratory conclusion.

The work described above gives some information in figures which one would intuitively expect, namely that a wind blowing against a clothed body would be more cooling in its effect than a wind blowing across the surface of the clothing. Taken in conjunction with figures in the writer's previous publication, they show, however, that this is more pronouncedly the case where the wind can blow through the sample into an air space underneath. The assessment of materials or combinations of materials in wind is therefore far from simple because it must depend on what is underneath; with an actual garment being worn this varies depending on whether it is lying smooth and tight or pouched and loose.

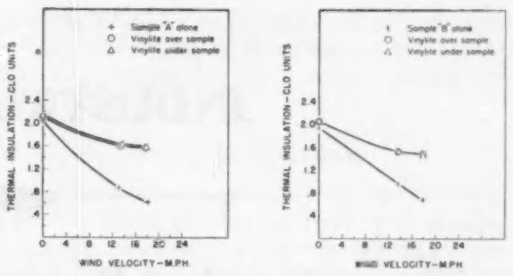

Fig. 3. Measurements of the thermal insulation of the A and B samples on the 45° plate in winds about 16 m.p.h. under conditions described in the text, using the clamping device.

Accordingly, some arbitrary but specified test is needed for winter outdoor garments in the interest of the manufacturer, the dealer, and the purchaser.

The writer favors a test over an air space on the 45° plate because this magnifies the deficiency of a sample in wind and because the plate is a less awkward piece of apparatus to handle than the cylinder.

A 45° plate test over an air space would not give a result in fundamental units, but for comparing samples and combinations of samples and for research and development work, this would in many cases not matter; such a test would eliminate quickly those samples which would give a wearer inadequate protection in cold windy weather. The most acceptable samples in a development program could be subjected subsequently to some more elaborate test if figures in fundamental units were demanded by some standardizing authority.

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INDUSTRIAL SECTION

Combed Roving Twist Formula

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Abstract

This study revealed that the twist required in rovings of combed cottons for good processing and drafting qualities varies directly with the hank roving, fiber fineness (Micronaire), and the variation of fiber length (both the uniformity ratio from the Fibrograph and per cent coefficient of variation from the Suter Webb Sorter). The twist varies inversely with the per cent noils removed and fiber length (Classer's staple length and upper half mean from the Fibrograph).

Four of these variables were incorporated into a formula, and a correction method was devised for the fifth variable. A nomograph based on this formula was constructed. It enables rapid determination of the twist required in rovings ranging from 0.25–10.0 hank, using combed cottons varying widely in fiber fineness, staple length, and per cent noils removed.

Introduction

In 1953, a carded roving twist formula was developed by members of this laboratory [4] for the purpose of providing mills with a yardstick for ascertaining the proper amount of twist to insert into their rovings for good drafting qualities and to save time in determining the correct twist when changing to a cotton differing in fiber properties. Since the amount of twist required in combed rovings for good drafting differs from the amount required in carded rovings, a similar formula for combed rovings was desirable. It is generally believed that this difference in required twist results from the combined effect of an increase in the average length of the fiber distribution and a higher degree of fiber straightness resulting from combing.

Although the effect of fiber properties upon the twist required in carded rovings has been studied by several experimenters [2, 4, 5, 6, 7], a survey of the English literature shows that there has been no empirical study of their effect upon the twist required in combed rovings. One study [3] estimates how the twist in combed rovings should vary from that in carded rovings when using the same cotton by advocating staple length plus $\frac{1}{8}$ in. when calculating twist for combed rovings. This would imply that all combed rovings would require less twist than carded rovings. While engaged in evaluating an extra long staple cotton at this laboratory, it was observed that coarse rovings from combed cotton required more twist than equivalent counts of roving from carded cotton of the same variety and staple length. This prompted an investigation to determine more precisely the effect of fiber properties upon the twist required in combed rovings and to develop a formula which would enable it to be quickly computed upon the substitution of these properties into the formula.

Instruments and Test Methods

The strength (obtained through twist) needed in both carded and combed rovings to insure good processing and drafting qualities depends to some extent on individual mill conditions. For example,

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if large size roving bobbins are being used, more strength would be required than when using small size bobbins. Moreover, if coarse yarn counts are being spun, the roving would revolve faster in the creel, thus requiring more strength than if fine counts were being spun from the same hank rovings. It has also been found that the strength needed in roving for good drafting qualities depends to some extent on the roll settings of the spinning frame. Therefore, in order to study the effect of fiber properties upon the twist required to produce the strength in roving for good processing and drafting qualities, it is necessary to use an instrument that indicates this strength for various hank rovings under average mill conditions. Such an instrument, the H and B [2] Belger Roving Tester, was the one used for this study.

The turns per inch in the rovings of the various cotton varieties referred to is *machine twist*, obtained by dividing the machine twist constant by the twist gear. Enough turns per inch were added to each hank roving so that the roving strength was that designated by the Belger Roving Tester for good processing and drafting qualities.

Cotton Varieties

The varieties of cottons used in the study with their respective fiber properties are listed in Table I. This group of cottons comprises a wide range in staple lengths and fiber fineness. All fiber properties were determined in accordance with test procedures as outlined by the American Society for Testing Materials [1].

[2] It is not the policy of the Department to recommend the products of one company over those of any others engaged in the same business. This name is furnished merely for your convenience and information.

Processing Procedure

The cottons were processed into rovings according to the best known practice (*i.e.*, type cards, productions, roll settings, etc.) for each variety and staple length. The processing machinery included the Saco Lowell [2] and Whitin [2] revolving flat cards and Whitin 4-roll drawing frame with cushion top rolls. For the combing operation a Whitin 11¾ in. width lap, sliver lapper, and a Whitin Model D4 comber were used. Seven rovings ranging from 0.50–6.00 hank were processed on the appropriate types of roving frames—10 × 5 in. Interdraft [2] and 8 × 4 in. Superdraft.[2]

The six cottons were processed into 40 gr./yd. first drawing sliver from 45 gr./yd. card sliver. Twenty-four ends of the first drawing sliver were converted into a sliver lap weighing approximately 700 gr./yd. Each cotton was combed into a 50 gr./yd. sliver with approximately 5, 15, and 25% noils removed. In addition to these percentages, the Wilds cotton had 10 and 20% noils removed. The combed slivers were processed through two processes of drawing, 50 gr./yd. sliver being made in each case. The drawing slivers of each cotton were processed into 1-, 3-, and 6-hank rovings. In addition to these, the Wilds was processed into 2-, 4-, and 5-hank rovings. Each hank roving produced was then tested for strength by the Belger Roving Tester.

TABLE I. Cotton Varieties and Fiber Properties

Cotton variety	Classer's evaluation		Fiber length and distribution						Micronaire unit*	Strength† Index	Maturity,†† %
			Fibrograph			Suter Webb					
	Length, in.	Grade	U.H.M., in.	Mean, in.	Uniformity ratio, %	25% Point, in.	Mean, in.	C.V., %			
Iquitos	1 1/16	Msp.	1.06	.85	.80	1.12	.97	23	7.12	6.8	97
Bobshaw	1 1/16	SM	1.06	.88	.83	1.16	1.00	24	5.00	8.1	92
Deltapine 15	1 3/32	SLM	1.02	.83	.81	1.12	.90	33	4.30	7.8	86
Stoneville 2B	1 1/16	M	1.08	.90	.83	1.16	.94	32	3.90	8.2	86
Wilds 13	1⅛	SMsp.	1.30	1.08	.75	1.40	1.17	30	3.80	8.1	86
Pima S—1	1 1/16	1½	1.37	1.16	.85	1.42	1.22	24	3.90	8.9	94

* Curvilinear scale.
† Pressley method.
†† NaOH method.

Results and Discussion

It was found in a previous study [4] that twist in carded roving varied directly with the square root of the fineness and inversely with the staple length. It was reasonable to assume that this function was as applicable to combed rovings as to carded rovings, since the preparatory drawing, the cutting, and the reworking of the cottons used in that study resulted in straight fibers comparable to combed fibers. This function of fineness and length was then assumed as a starting point in the derivation of an equation for calculating combed roving twist.

The effect of roving hank on the turns per inch in roving was found by plotting these values against each other for all cottons. This is shown in Figure 1 for the six cottons with approximately 15% noils removed. Similar plots were made for these cottons with 5 and 25% noils removed, but are not shown here. Since the plot of six rovings from the Wilds combed cotton gave a parabolic curve like the carded rovings in two other studies [2, 4] it was assumed that similar plotting of the values of hank rovings and turns per inch from other cottons, either combed or carded, would yield parabolic curves. With this in mind, and the fact that the scatter of points along the curves for the Wilds cotton of the current study and the carded cottons of other studies [2, 4] were not very great, three points and the origin were considered adequate to form the curves for empirically establishing the effect of hank on combed roving twist. The origin can be considered as a point because theoretically a roving of infinite weight would require zero twist.

These curves were found to be of the type

$$Y = K_1(H.R.)^n \qquad (1)$$

where Y = turns per inch, $H.R.$ = hank roving, K_1 = a constant, and n = a constant. The value K_1 is constant for any one cotton but differs with cottons of different lengths or finenesses. When the specific equations of this general equation were calculated for the six cottons of each noil removal, the values of n varied between 0.52 and 0.66, with the average being approximately 0.60. This indicates that the twist for combed rovings varies directly with the hank roving to the 0.60 power. This differs slightly from carded rovings, where it was found that twist varied directly with hank roving to the 0.67 power. This indicates that as the hank changes the necessary rate of change in twist is greater for the carded than the combed rovings.

The effect of per cent noils removed upon the turns per inch in roving for the six cottons and the three roving counts [3] is shown in Figure 2. It is noticed that the plots of these values form straight line relationships with negative slopes. The intercepts for the extrapolation of these lines on the ordinate indicate the amount of twist for combed rovings with zero noils removed.

Based on the first assumption and the relationships revealed in Figure 1, it is now indicated that the twist in combed rovings varies directly with the square root of the fineness and hank roving to the 0.60 power, and inversely with staple length. That is

$$Y = \frac{K_2(F)^{0.50}(H.R.)^{0.60}}{L} \qquad (2)$$

where K_2 = constant, F = Micronaire fineness (curvilinear scale), and L = staple length.

The value of K_2 was found by substituting the values of F, $H.R.$, and L of the cotton varieties into

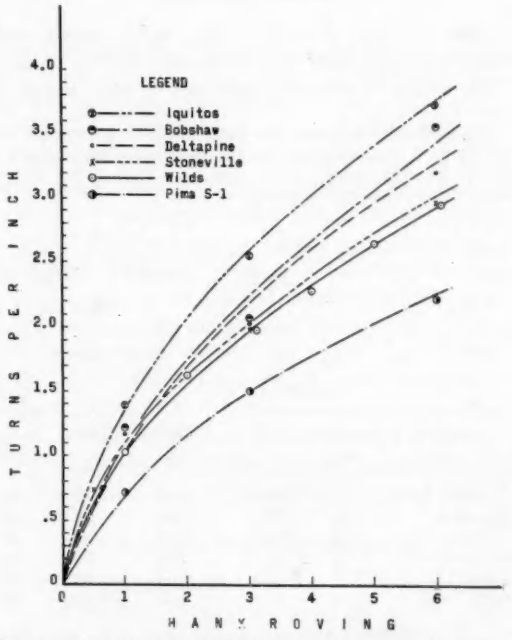

Fig. 1. Effect of hank roving on the turns per in. in roving for six cottons with a 15% noil removal.

[3] There was insufficient stock to produce the 1.00 hank roving from the Stoneville 2B.

Equation 2 and equating it to their respective intercepts, as obtained from Figure 2. The intercepts and slopes of the lines from Figure 2 and the values of K_2 are shown in Table II. The average value of K_2 for the three roving counts and six varieties is 0.60. Therefore, the twist formula for combed rovings with zero noils removed is

$$Y = \frac{.60(F)^{0.50}(H.R.)^{0.60}}{L} \qquad (3)$$

It is generally recognized that the upper half mean length obtained by the Fibrograph is a more accurate measure of length than classer's length. However, since many mills do not obtain Fibrograph data on their cottons, the formula was developed on the basis of classer's length. In order to test the formula for use with Fibrograph measurements, the upper half means of these cottons as obtained by the Fibrograph (Table I) were substituted into Equation 2 in place of staple lengths, and K_2 was calculated to be 0.595, which for all practical purposes is the same as found when using staple length (0.60). This indicated that, for the cottons included in this study, the value of upper half mean and staple length can be interchanged without affecting the accuracy of this empirical formula. Had the values of K_2 been calculated for cottons differing in fiber properties from those used in this study, it is possible that the value calculated with the use of Fibrograph measurements would have differed somewhat from that calculated with the use of classer's length.

It is evident from the negative slope of the lines in Figure 2 that, as the amount of noils removed is increased, the twist required in the rovings is decreased. It is also evident from the average values listed in Table II that this negative slope increases with an increase in roving count.

These average values of slope were plotted against their respective hank rovings and connected by a curve. The origin can also be considered a point in this instance because, regardless of the finite percentage of noils removed, the remaining mass is infinite and the twist will be unaffected. A parabolic curve was fitted to these points by a modified method of averages. The equation was calculated as

$$s = -0.0037(H.R.)^{0.7} \qquad (4)$$

where s = slope. The equation of the lines in Figure 2 is

$$Y = a + b(P.N.) \qquad (5)$$

where a = the right hand member of Equation 3,

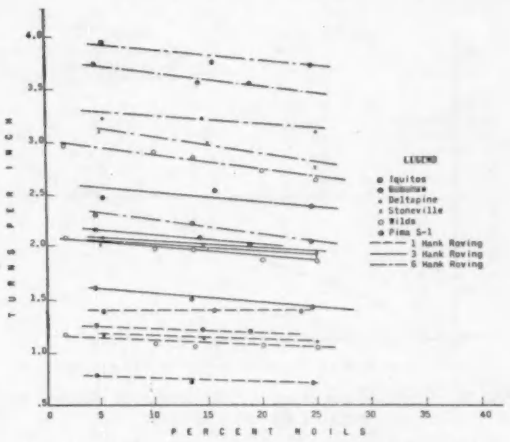

Fig. 2. Effect of per cent noils upon the turns per in. in roving.

TABLE II. Values of Slopes and Intercepts from Figure 2 and the Constants K_2 Calculated from These Intercepts

	Hank roving								
	1.00			3.00			6.00		
	Slope	Intercept	K_2	Slope	Intercept	K_2	Slope	Intercept	K_2
Iquitos	.000	1.38	.55	−.010	2.61	.52	−.011	3.96	.54
Bobshaw	−.005	1.26	.59	−.010	2.22	.54	−.013	3.80	.61
Deltapine 15	−.004	1.19	.61	−.006	2.12	.56	−.009	3.32	.58
Stoneville 2B*				−.006	2.08	.580	−.019	3.20	.59
Wilds 13	−.004	1.13	.72	−.009	2.09	.69	−.014	3.00	.65
Pima S-1	−.003	.80	.58	−.010	1.66	.62	−.014	2.40	.59
Average	−.0032		.61	−.0085		.59	−.0133		.59

* Insufficient stock to produce 1.00 hank roving.

b = slope = right hand member of Equation 4, and $P.N.$ = per cent noils.

The equation for twist in combed rovings with any per cent of noils removed becomes

$$Y = \frac{.60(F)^{0.50}(H.R.)^{0.60}}{L} - 0.0037\ (H.R.)^{0.7}(P.N.) \quad (6)$$

The turns per inch as calculated by this formula were checked against the actual turns per inch for 1-, 3-, and 6-hank rovings (approximately 15% noils removed) for the cotton varieties used in this experiment and all other varieties that were combed at the laboratory prior to the experiment. The values for the 1-, 3-, and 6-hank rovings are listed in Table III, along with the per cent error. The per cent error is the percentage deviation of the actual turns per inch from the calculated turns per inch.

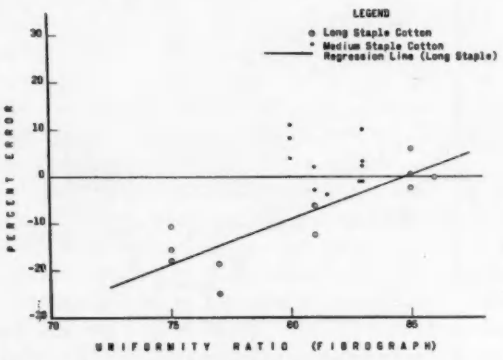

Fig. 3. Effect of variation of fiber length on the per cent error of the twist formula.

The values as listed in the table indicate a good agreement between the turns per inch as calculated by the formula and the actual turns per inch except for the Wilds, Karnak, and Pima 32 cottons. The average per cent error for each hank roving of all cottons is within an acceptable range for roving twist formulas. It was observed that the largest errors occurred with long staple cottons of high length variability (Karnak, Pima 32, and Wilds). These cottons required more twist than the amount advocated by the formula. In order to ascertain if the variability of fiber length was related to the per cent error, the uniformity ratios (Fibrograph) were plotted against the per cent error, as seen in Figure 3. The values for only one lot of the Pima S-1 cotton were used. This plot reveals that there is no apparent relation between per cent error and uniformity ratio for the medium staple cottons. There appears to be a definite relationship between these variables for the long staple cottons. It is observed that the range of Fibrograph values for the medium staple cottons is only from 0.80 to 0.83, while for the long staple cottons it is from 0.75 to 0.86. However, the range of per cent C.V. of length (Suter Webb) of both the long and medium staple cottons was approximately the same, and a plot of these values yielded the same relationships as observed here. The long staple cottons of low uniformity ratios have high per cent errors on the minus side, indicating that they require more twist than advocated by the formula. The regression line for the

TABLE III. Values of Twist as Calculated by Equation 6; Actual Values and the Percent of Error

	1.00 Hank roving			3.00 Hank roving			6.00 Hank roving		
	Turns/in.			Turns/in.			Turns/in.		
Cotton	Calc.	Actual	% Error	Calc.	Actual	% Error	Calc.	Actual	% Error
Iquitos	1.45	1.39	4.14	2.78	2.54	8.63	4.22	3.74	11.37
Bobshaw	1.21	1.22	−.83	2.33	2.09	10.30	3.52	3.55	.85
Deltapine 15	1.09	1.13	−3.67	2.08	2.03	2.40	3.15	3.23	−2.54
Stoneville 2B				2.03	1.98	2.46	3.08	2.97	3.57
Wilds 13	.89	1.05	−17.98	1.71	1.98	−15.78	2.56	2.84	−10.94
Pima S-1	.77	.72	6.49	1.48	1.51	−2.02	2.24	2.22	.89
SXP							2.03	2.03	0
Karnak				1.32	1.65	−25.00	2.00	2.37	−18.5
Pima 32				1.29	1.45	−12.40	1.97	2.09	−6.09
Pima S-1*	.77	.72	6.49	1.46	1.45	.68	2.22	2.22	0
Absolute average			6.60			8.85			5.48

* Taken from a previous lot of combed stock. The 6.00 hank roving was processed from roving on a 7×3 in. roving frame.

uniformity ratio and per cent error as calculated for the long staple cottons was:

$$\% \text{ Error} = -157.63 + 1.85 \text{ (Uniformity Ratio)} \quad (7)$$

If the uniformity ratio is known, the per cent error for long staple cottons of high length variability could be calculated by Equation 7, and an adjustment in the turns per inch as calculated by Equation 6 could be made.

No doubt many other variables such as fiber friction, convolutions, maturity, etc., affect twist to a lesser extent than those studied here. Due to the complexity of such an equation, it does not seem advisable to try to include them in an empirical formula.

A nomograph (Figure 4) based on Equation 6 was constructed by standard techniques [8]. This nomograph enables rapid determination of the turns per inch of twist required in rovings ranging from 0.25 to 10.0 hank from combed cottons varying widely in fiber fineness and staple length. This tool should assist mills to decide to what extent their present roving twist is hard or soft. It should also help to eliminate the guesswork in determining the twist when changing to a cotton with different fiber properties.

Nomographs ($8 \times 10\frac{1}{2}$ in.) are available, without charge, from the Southern Regional Research Laboratory, 1100 Robert E. Lee Boulevard, New Orleans 19, Louisiana.

Conclusions

From this study it is concluded that the twist required in combed roving for good drafting qualities varies with the following properties in the following manner:

1. Hank roving—directly
2. Classer's staple length and upper half mean length (Fibrograph)—inversely
3. Micronaire fineness—directly
4. Per cent noils—inversely
5. Coefficient of variation of fiber length—directly.

Four of the most important of these variables have been incorporated into an empirical formula, and a correction method has been derived for the fifth for use with long staple cottons of high length variability.

It was also indicated that the twist required in coarse hanks is greater for the combed rovings than for the carded, while in very fine hanks a reversal of this condition is common. This can be shown by comparing Formula 6 with the carded roving twist formula of the previous study [4]. The turns per inch required in a 1.00 hank roving of carded cotton with a staple length of $1\frac{1}{4}$ in. and a Micronaire fineness of 4.00 would be 0.80. For the same roving, combed with a 15% noil removal, it would be 0.91. The turns per inch would be 2.64 and 2.61 respectively for a carded and combed 6.00 hank roving.

Acknowledgment

The authors wish to express their appreciation to Mr. C. L. Sens, Supervisor of the Processing Unit,

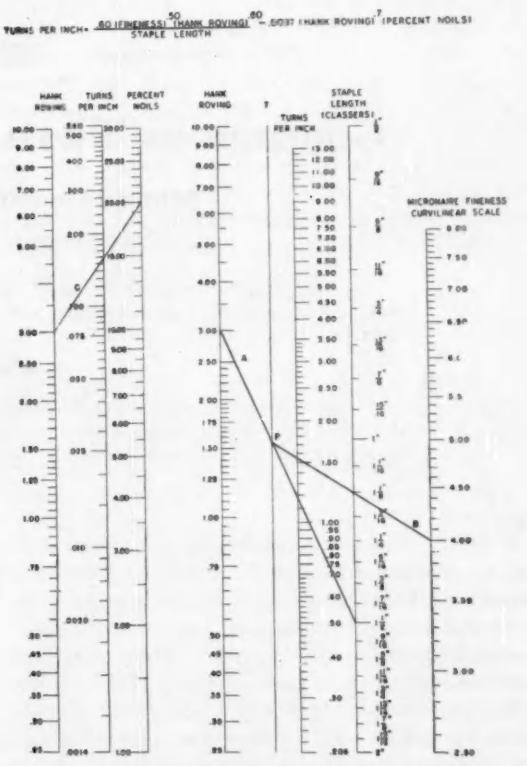

Fig. 4. Nomograph. Key: assume a 3.00 hank roving with cotton of a staple length of $1\frac{1}{2}$ in., a fineness of 4.00, and a noil removal of 20%. Connect the hank roving with the length (line A), intersecting line T at point P. Connect this point with the fineness (line B). This line will intersect the twist line at the correct turns per in. for the roving with zero % noils removed − 1.54. On the adjacent chart connect hank roving with the per cent noils (line C). This line will intersect the twist line at the turns per in. that should be subtracted from that for zero % noils (1.54 − .16 = 1.38), and will give the required turns per in.

Cotton Mechanical Processing Section, for his general supervision of the study and for his many helpful comments in evaluating the data and preparing them for presentation; to fellow members of the Cotton Mechanical Processing Section for processing the cotton into rovings and making the twist determinations; and to coworkers of the Textile Testing Unit of the Analytical, Physical-Chemical, and Physics Sections for fiber property determination.

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Continuous Twist Irregularity Tester

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In this paper is presented a novel idea. In spite of obvious limitations to the techniques described, it is interesting and stimulating in a potentially important area. EDITOR.

Abstract

Three types of continuous twist irregularity testers were constructed which measure the variability of twist along a specified length of yarn utilizing a continuous untwist-twist principle. These testers can also be used to detect periodicities.

VARIOUS evenness testers are now widely used to measure variations in the weight and diameter distributions per unit length of yarns and slivers. But the writers are aware of none that measures twist irregularity continuously, except one trial method, described by Gonsalves [2], which utilizes the change in the intensity of a light passing by the side of a strand. This is, however, applicable only to cords and continuous filament yarns which are less fluffy than single cotton or woolen yarns. This paper deals with three types of twist irregularity testers which were constructed in an attempt to measure automatically the twist variation for yarns both of continuous filaments and of staple fibers by the application of the principle of untwist-twisting as recommended in ASTM [1] for determining the t.p.i. of twist for a yarn.

By utilizing the untwist-retwist method, Magni [3] constructed a twist tester on which the specimen was tested without being cut. But he used the device for comparing only the twist number on this tester with that on the usual one. The continuous testers described below, however, can draw the twist irregularity curve on the recording paper, thus eliminating all the human error due to cutting and setting the specimen intermittently, and facilitating the twist control activities.

Continuous Twist Irregularity Tester, Type A

The construction of the Type A tester is shown in Figure 1, where a disc (1), driven by motor (2), has a pair of freely rotatable twist rollers (3) and (3′). The bearings of one roller are fixed on the disc, but those of the other roller can move freely to give an

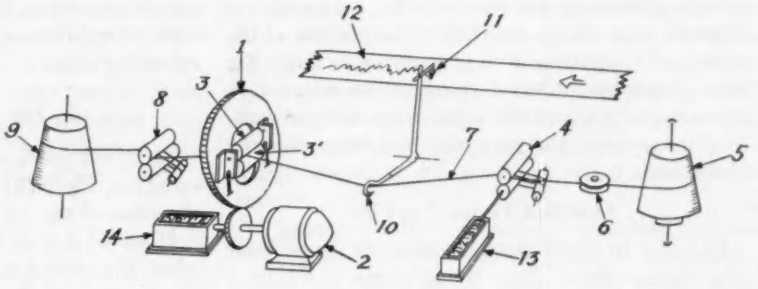

Fig. 1. Twist irregularity tester, Type A.

appropriate pressure on each roller. Therefore, the rotating disc is able to twist yarn without hindering its passage through a hole at the center of the disc. Feed rollers (4) draw yarn from the bobbin (5) through the tension compensating device (6) by winding the specimen three times around a skewed roller and feed rollers to get the accurate feed under constant tension. Take-up rollers (8) have the same construction and rotate with the same surface speed as feed rollers. The package (9) is frictionally driven. If a light lever (10) is put on the running yarn at the center between the feed rollers (4) and disc (1), the pen (11) attached on the other end of the lever (10) describes a horizontal line on recording paper (12) when the disc (1) does not revolve. But if it is rotated in the proper direction, the lever first goes down by the untwist of yarn and then comes up due to the twist contraction. When the rotation of the disc is adjusted by a variable speed mechanism to a settled speed so that the pen may move along a roughly horizontal line, a record of the twist variation of the specimen is drawn on the paper. The yarn after test has almost the same t.p.i. in the same direction as the yarn before test, and, if wanted, may be put in the production line for subsequent processings.

The mean t.p.i. of twist can be obtained when the total number of revolutions of the disc, measured by the revolution counter (14) attached to the disc, is divided by the tested yarn length, measured with the yard meter (13) connected to feed rollers.

The specimen between feed rollers and twist rollers is partially and continuously untwist-twisted, and never becomes twistless. Therefore it may be assumed that there is no increase in yarn length due to the slippage between fibers, whether continuous filaments or staple fibers. The same is true also of the yarn between twist rollers and take-up rollers. Therefore the only factor relating to the length change of the yarn due to twisting is the twist contraction coefficient (in./in.-turn), which varies according to the t.p.i. of twist given to the yarn. In this case, the number of turns of twist per inch of the yarn between feed rollers and twist rollers is roughly kept constant; only the twist contraction coefficients α and β, that are observed when the specimen just regains its original length after the first and second untwist-twist operation respectively, have relation to the mathematical formula on which the operation of this device is based. Derivation of the formula for the Type A Tester is given in Appendix A, which shows

$$\frac{\partial a}{\partial t} = 2a\alpha v(\bar{N} - N_a) \qquad (1)$$

where, referring to Figure 2, a = yarn length between feed rollers and twist rollers (in.), $\bar{N}$ = mean of t.p.i. of yarn incoming to region a, N_a = t.p.i. of yarn in region a, v = yarn running speed (in./min.), and t = time (min.). Hence the change of turns of twist can be determined by the slope of the curve on the recording paper.

This tester has a nip point of feed rollers as the starting point of test region a. Therefore, no turns of twist inserted by the twist rollers can be transmitted backward from the test region a through the feed rollers. This is a principal merit of the Type A tester, and it is best applied to a specimen which is slippery, such as silk or highly twisted (as in crepe) yarn. The machine has the following inevitable defects: (1) The displacement of the pen on the

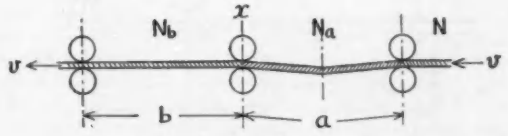

Fig. 2. Symbols for the tester.

recording paper is not linear to Δa, thus giving a different slope value according to the position of the lever, and (2) when the twist variation is large, the lever goes down too low to transmit the twist-roller-rotation uniformly to the incoming part of the yarn. In extreme cases, the yarn may be broken near the feed rollers.

Modified Tester, Type B

In order to avoid these troubles, the pendulum-type device termed Type B and shown in Figure 3 is applicable. Two feed rollers (1) contact each other horizontally, passing the yarn vertically down to the tension roller (2). The specimen then passes horizontally through twist rollers (3) to take-up rollers (4). The arm mounting the tension roller is pivoted at the point (6), where two feed rollers contact each other. Thus a smaller displacement of the tension roller does not change the yarn length between the roller (2) and the point (6). Equation 1 applies also in this case.

Now, letting m = ratio of the yarn speed v to the running speed of the recording paper, and n = magnification ratio of the pen movement to the tension roller displacement, we have the slope s on the recording paper:

$$s = 2mna\alpha(\bar{N} - N_a) \qquad (2)$$

As all the coefficients outside the parentheses are constant, the twist variation can be measured by the slope of the curve on the recording paper.

If we let $s = dy/dz$, we have $y = \int s\,dz$. Thus, when the recorded curve is cut at heights y_1, y_2, . . . with many lines parallel to the y-axis, evenly spaced at distance h, $(y_1 - y_2)/h$, $(y_2 - y_3)/h$, . . . indicate the mean slopes for the yarn length mh. The twist variation calculated in this way has the same meaning as the CV value obtained with the usual untwist-twist method when mh is equal to 10 in.

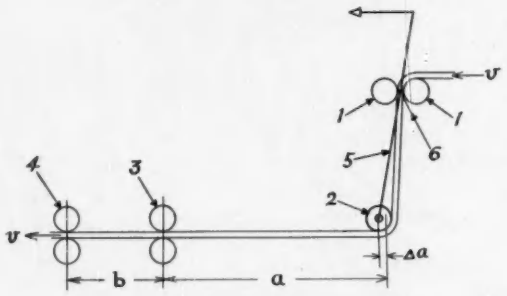

Fig. 3. Twist irregularity tester, Type B.

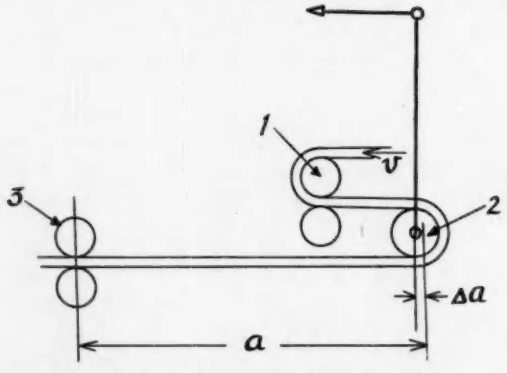

Fig. 4. Twist irregularity tester, Type C.

Modified Tester, Type C

Even the Type B tester cannot eliminate the scale-out of the pen when testing a relatively long length of yarn having either more or less twist than the average, because the pen integrates the difference in twist contraction between the test length and the mean. The device termed Type C and shown in Figure 4, on the other hand, has a self-compensating character. The yarn passes backward from feed rollers (1) to a tension roller (2), then makes a U-turn to the normal running direction. When the less twisted part of yarn comes into test region a, it is twisted more due to the untwist-twist, and contracts Δa, causing the leftward displacement of the tension roller by the same amount. This adds the negative turns of $2\Delta aN$ to the yarn a, helping to keep the yarn twist in region a as constant as possible. The converse is also true.

The formula on which the operation of this tester is based is as follows:

$$s = \frac{2mna\alpha}{1 + 2a\alpha\bar{N}}(\bar{N} - N_a) \qquad (3)$$

The derivation of the formula is given in Appendix B.

Observed Irregularity Curves

One of the curves obtained on the Type A tester with cotton 20's single yarn is shown in Figure 5A. The lines indicating 2, 4, 6 . . . % do not represent the twist-irregularity percentages, but show the percent elongation of the yarn in the test region.

Since the distances between these lines are not equal, various scales should be used to measure the slope of the curve.

Figure 5B is one of the examples tested on the Type B tester with the same yarn, but with much faster chart speed. By Equation 2, the maximum variation in any section is calculated as follows:

$$\text{Max. V} = \frac{1}{2mna\alpha\bar{N}} (s_{pos} + s_{neg})$$

where s_{pos} and s_{neg} are the maximum positive and negative slopes in a section. For instance, in the first 10-in. section in Figure 5B, the maximum V is:

$$\text{Max. V} = \frac{1}{2 \times 5 \times 3.7 \times 10 \times 0.00815 \times 17.24 \times (3.13 + 3.00)}$$

$$= 11.6\%$$

where 0.00815 and 17.24 are the values of α and $\bar{N}$ respectively. The next maximum V is 10.8%. Averaging many of these values, the mean maximum twist variation for this yarn is obtained.

Figure 5C shows a long-term twist variation on the Type C tester with the same yarn. Rather marked periodical variation having the wave length of 11.2 in. can be observed, a similar tendency being seen also in Figure 5A. By cutting the curve of Figure 5C at 10-in. intervals, the twist variation is calculated as CV = 1.76% by the following formula:

$$N_a = \bar{N} - \frac{1 + 2a\alpha\bar{N}}{2mna\alpha} \left(\frac{y_i - y_{i+1}}{h} \right) \qquad (4)$$

The value, 1.76%, seemed much smaller than that found by the usual twist testing. This may be because the latter is calculated with samples cut at random along the yarn. If the cut length does not coincide with the wave length of the twist irregularity, it shows a much larger twist variation than when it does coincide. In the case of Figure 5C, the wave length is barely longer than the cutting space, so that a smaller value is obtained for the twist variation. This suggests that careful consideration should be paid in determining the gauge length of the specimen when the twist is tested.

Figures 6A and 6B show twist irregularity curves for cotton 60's/2 and worsted 48's/2 respectively, tested on the Type C tester with 10-in. gauge length.

Reproducibility of Results

When the specimen passes through the above-mentioned devices, it is partially untwist-twisted twice, first between feed rollers and twist rollers, then between twist rollers and take-up rollers.

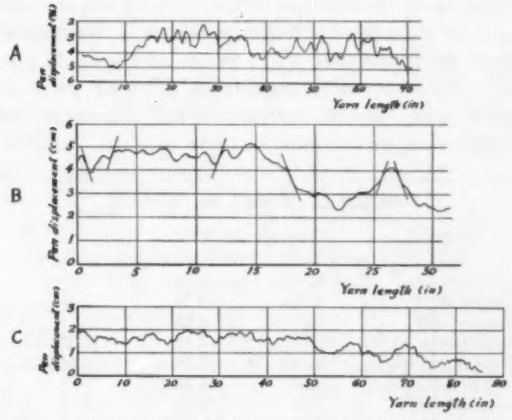

Fig. 5. Twist irregularity curves of cotton 20/1; (*A*) on Type A tester, a = 5 in., m = 12.4, n = 3; (*B*) on Type B tester, a = 10 in., m = 5, n = 3.7; (*C*) on Type C tester, a = 10 in., n = 12.4, n = 6.

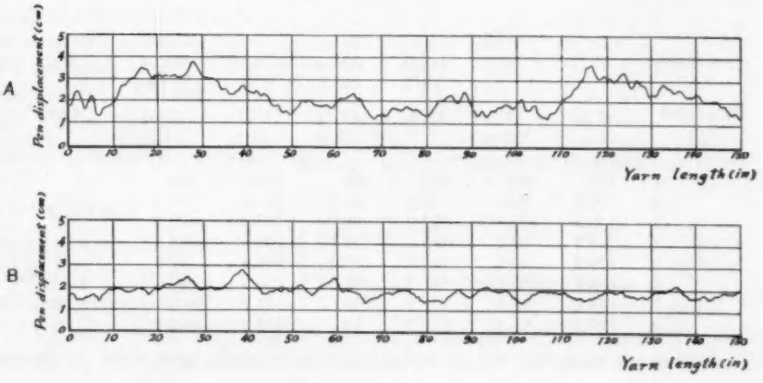

Fig. 6. Twist irregularity curves on Type C tester; (*A*) cotton 60/2, m = 12.4, n = 9.5; (*B*) worsted 36/2, m = 3.7, n = 9.5.

Therefore, both the uniformity and constancy of α and β are concerned with the reproducibility of the twist variation curve.

To study this constancy, specimens were untwist-twisted on a common type of twist tester with 10-in. gauge lengths for eight cycles. The total revolutions of the rotatable clamp were read each time when the specimen regained its original length. As the elongation allowed for the untwisted yarn has some relation to the measured twist, it was determined to be 1.25%, except for 120 den. rayon which had been preliminarily steam set for 10 min. (2.5%).

The results are shown in Table I. They were averaged with twenty samples per yarn cut at random and tabulated as the ratio T_n/T_1, where T_n is the total number of revolutions for the necessary untwist-twist in the nth cycle. The table shows that the yarn consisting of staple fibers always increases in length when it is untwisted, with the result that T_n increases as the cycle goes on. However, with continuous filament yarns or plied yarns (except worsted 36's/2) T_n decreases, chiefly due to the bulk increase of yarn diameter. This decrease is observed only for the first cycle; in the following untwist-twists the T_n is nearly constant. The increase of T_n in worsted 36's/2 and rayon 120 den. after the second cycle may be because the crimps in them are lost successively under the repeated stretching.

As the ratios are not constant, the twist contraction coefficients α and β are always changing, making it difficult to reproduce the same twist irregularity curve even when the same specimen is tested. One of the examples is shown in Figure 7 with cotton 20's/1 yarn.

Uniformity of α and β

The formulas already mentioned are derived under the assumption that α and β are uniform along the yarn. To check this, specimens are tested for 10-in. gauge lengths on the above-mentioned twist tester. The coefficients α and β are then determined by the slopes of twist contraction curves at points where the specimen regains its original length at the first and second untwist-twist cycles. In Table II are tabulated these α and β, calculated by the least square method and averaged with twenty samples taken at random along the yarns. As each yarn has the CV of several percentages, the twist variation is affected by this error, which is roughly equal to the CV of the twist irregularity. Therefore, the above-mentioned testers cannot measure separately the twist variation if the uniformity of α and β is not assumed. However, the assumption that α and β are uniform along the yarn would be acceptable, as the usual

TABLE II. α and β (in./in.-turn)

Material	Average ($\times 10^{-3}$)		CV, %	
	α	β	α	β
Cotton 20/1	8.15	8.56	7.28	7.37
Cotton 30/2	6.04	5.66	7.21	5.53
Spun rayon 20/1	6.83	7.35	6.27	7.64
Spun rayon 60/2	4.37	7.26	6.44	6.25
Worsted 36/2	9.69	7.26	6.44	7.51
Viscose rayon 120 den.	3.99	4.06	3.03	3.74

TABLE I. Ratio of T_n/T_1

Specimen		Ratio						CV of ratio, %					
		Cotton 20/1	Cotton 30/2	Spun rayon 20/1	Spun rayon 60/2	Worsted 36/2	Viscose rayon 120 den.	Cotton 20/1	Cotton 30/2	Spun rayon 20/1	Spun rayon 60/2	Worsted 36/2	Viscose rayon 120 den.
Initial** t.p.i.		17.2s	17.8s	13.9s	21.1s	11.2s	43.6s	5.0*	3.3*	5.8*	14.2*	6.6*	4.4*
			20.4z		29.5z	13.1z	41.2z		1.0		7.1	11.3	3.8
Cycle number	1	100	100	100	100	100	100	0	0	0	0	0	0
	2	104.1	94.8	100.5	96.5	101.4	96.5	2.67	1.12	1.32	1.79	1.32	0.86
	3	112.5	95.9	103.6	98.0	103.4	97.8	2.93	1.28	1.78	1.86	1.59	1.25
	4	119.7	95.2	105.4	97.5	104.5	98.2	4.51	1.62	2.34	1.27	1.44	2.22
	5	128.2	95.8	109.1	98.3	105.9	99.0	4.95	1.37	2.85	1.67	1.90	1.08
	6	135.4	95.6	111.2	98.2	106.7	99.6	5.26	1.75	3.21	2.03	2.08	0.89
	7	143.0	95.9	114.3	98.5	107.7	100.1	5.78	1.83	3.77	2.90	2.28	0.95
	8	149.5	95.6	116.3	98.6	108.5	100.8	5.66	1.66	4.28	2.79	2.15	1.08

* CV (%) of the initial t.p.i. ** Upper line = single twist, lower = ply. s and z indicate direction of twist.

untwist-twist method to determine the twist number of yarn is based on a similar assumption.

Discussion

In some cases a marked periodical twist variation was observed, which makes the calculated twist variation vary considerably according to the gauge length. Therefore, it should be considered whether or not it is appropriate in such a case to use the usual 10-in. gauge length.

In order to calculate the true twist variation from the curve obtained, the twist contraction coefficients must be observed first. But in the mill, where similar quality of yarn is produced daily from nearly uniform stock, the successive product may be considered to have the same contraction coefficient. Even if the coefficient is unknown, by comparison of the daily curves by these testers one can find a great help in the quality control of spinning and throwing processes.

Summary

Three types of twist irregularity testers for measuring twist variation by a partial and continuous untwist-twist method were studied. Because the twist contraction coefficients change according to the untwist-twist cycles, the reproducibility of results on these testers is not as good as one could wish. However, they may be successfully used for the daily twist control. In some cases the observed curves showed marked periodical variations. This indicates it is necessary to select an appropriate gauge length to get an acceptable estimate of the twist value.

Acknowledgment

The authors wish to express their appreciation to Mr. D. S. Hamby for his genial encouragement, and to Messrs. K. Nakajima, Y. Miura, and H. Noshi for their valuable suggestions. Special indebtedness is expressed to K. Fujiki, H. Oka, and T. Nagai for assistance in this experiment.

Appendix A: Derivation of Equation 1

Referring to Figure 4, a = original yarn length between feed rollers and twist rollers (in.), b = distance between the centers of twist rollers and take-up rollers (in.), N = t.p.i. of yarn incoming to region a, N_a = t.p.i. of yarn in region a, N_b = t.p.i. of yarn in region b, x = r.p.m. of the rotating disc, v = yarn running speed (in./min.), and α and β = twist contraction coefficients after the first and second untwist-twist cycles, respectively (in./in.-turn). The change of turns of twist, ΔN_1, after short time Δt for yarn b may be written

$$\Delta N_1 = x\Delta t - v\Delta t N_b - (v\Delta t + b\beta\Delta N_1)N_a$$

Here the first term, $x\Delta t$, represents the added turns of twist with twist rollers, the second term, $v\Delta t N_b$, being the turns of twist removed due to the running of yarn, and the fourth term, $b\beta\Delta N_1 N_a$, indicating the effect due to the contraction of yarn b. Therefore,

$$\Delta N_1 = \frac{\Delta t}{1 + b\beta N_a}(x - vN_b - vN_a) \qquad (a)$$

With yarn a, its original length a and total twist aN_a are assumed to have changed to $a - \Delta a$ and $aN_a + \Delta N_2$ after a short time Δt. Thus

$$\Delta N_2 = x\Delta t - (v\Delta t + b\beta\Delta N_1)N_a - v\Delta t N \qquad (b)$$

Substituting ΔN_1 from (a) into (b)

$$\Delta a = \frac{a\alpha\Delta t}{1 + b\beta N_a} \times [x - vN_a - vN + b\beta N_a v(N_b - N)] \qquad (c)$$

If the disc rotation is kept at a constant speed of $x = 2\bar{N}v$ ($\bar{N}$ is the mean value of N), the values within the bracket are $v\{(\bar{N} - N) + (\bar{N} - N_a) + b\beta N_a(\bar{N} - N)\}$. As was explained in the body of the paper, β is very small; therefore the third term is negligible when b is sufficiently small. On the other hand, due to the continuity of the twist distribution, N can be assumed roughly equal to N_a in time Δt. Therefore, the simplified formula is $\Delta a = 2a\alpha v(\bar{N} - N_a)\Delta t$, or

$$\frac{\partial a}{\partial t} = 2a\alpha v(\bar{N} - N_a) \qquad (1)$$

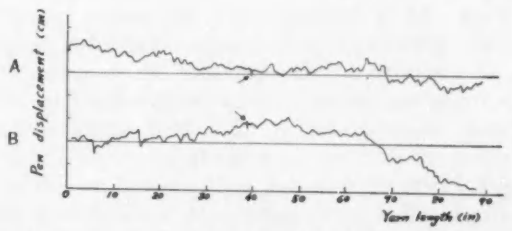

Fig. 7. Repeated twist testing of cotton 20/1; (*A*) first testing; (*B*) second testing. Arrows show the knot-place.

Appendix B: Derivation of Equation 3

Changing (b), the formula reads

$$\Delta N_2 = x\Delta t - (v\Delta t + b\beta\Delta N_1)N_a - (v\Delta t + 2\Delta a)N \quad (d)$$

where $v\Delta tN$ = turns of twist removed by the running of yarn, and $2\Delta aN$ those removed by the displacement of the tension roller. Substituting (a) into (d),

$$\Delta a = \frac{1}{1 + 2a\alpha N} \times \frac{a\alpha\Delta t}{1 + b\beta N_a} \times [x - vN_a - vN + b\beta N_a v(N_b - N)]$$

Letting $x = 2\bar{N}v$, and neglecting the terms representing small quantities,

$$\Delta a = \frac{2a\alpha v}{1 + 2a\alpha N}(\bar{N} - N_a)\Delta t \quad (e)$$

Substituting $\bar{N}$ for N in the denominator, as the twist change is generally small; the approximate formula is

$$s = \frac{2mna\alpha}{1 + 2a\alpha\bar{N}}(\bar{N} - N_a) \quad (3)$$

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Manuscript received September 26, 1957.

Letters to the Editor

Short communications in the form of Letters to the Editor are intended to provide prompt publication of significant new research results and to permit an exchange of views on papers previously published in the Journal. These communications are not submitted to formal review as are research papers, and the editors do not assume any share of the author's responsibility for the information given or the opinions expressed. When work previously published in the Journal is the subject of critical comment, the authors of the original paper are given an opportunity to submit a reply, which will be published concurrently when possible.

Automatic Ignition and Timing of the Flame in the Vertical Fire Resistance Test

Southern Regional Research Laboratory [1]
New Orleans, Louisiana
March 31, 1957

To the Editor
Textile Research Journal

Dear Sir:

The vertical fire resistance test has met with considerable acceptance for determining the efficacy of flame retarding finishes [1, 2, 3]. The test consists essentially of exposing the test fabric to a Bunsen flame for exactly 12 sec. under prescribed conditions and noting particularly the duration of the flaming and the length of char produced. Although the reproducibility depends to a large extent on accurate control of the exposure time, the procedure for accomplishing this purpose has been left largely to the operator. One of the procedures cited makes no mention of ignition techniques [2], another calls for a pilot light attached to the burner [1], while the third permits either a "pilot attachment or a manipulating bar for lighting" [3]. Rowley and Sonnino reported work on controlling the gas pressure and employed electrical timing of the flame, but used a pilot light for ignition [4].

Experience has shown that the heat rising from the pilot flame tends to bias the results—in some fabrics, even scorching has been observed. A manipulating bar is awkward and its use does not solve the problem of timing.

A practical solution has been developed which eliminates the pilot flame and controls the gas flow automatically, thus allowing the operator to give undivided attention to the flaming characteristics of the test specimen. Although the components required are for the most part readily available, appropriate substitutes should perform equally well. The essential elements used are a high voltage transformer to supply spark ignition and a timer and solenoid valve for controlling the gas supply for a predetermined interval. A schematic diagram showing the circuit is presented in Figure 1.

A Time-O-Lite [2] 0–60 second photographic timer, slightly modified as described below, controls the open time of the solenoid-operated gas valve. The timer was modified by mounting a Microswitch beneath the start button in such a way that it closes slightly before the timer-operated switch which opens the solenoid valve. Thus, slightly before the beginning of the time interval, the ignition transformer [3] is energized by the line voltage and furnishes about 5000 volts to an electrode placed slightly above and about $\frac{1}{32}$–$\frac{1}{16}$ in. from the rim of the Bunsen burner. Upon releasing the start button the ignition spark stops, although the solenoid valve remains open for the predetermined time.

The electrode was made from a demountable auto-

[1] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

[2] Mention of trade names does not imply their endorsement by the U. S. Department of Agriculture over similar products not mentioned.

[3] Gardner STJ 12, 115–10,000 v., center tapped, Gardner Electric Co., Emeryville, California.

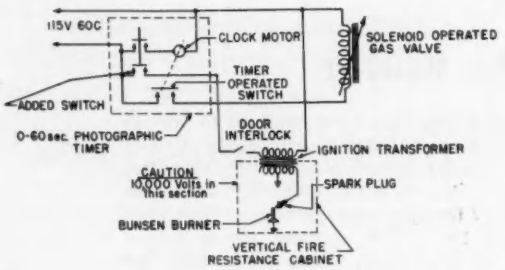

Fig. 1. Circuit diagram for automatic ignition and timing of flame in the vertical fire resistance test.

mobile spark plug after discarding the threaded body and retaining only the porcelain insulated electrode, which may be supported easily. A spark plug of this type is the English KLG, which is used in imported automobiles. In order to minimize insulation difficulties, the high voltage conductor is a standard spark plug wire, supported only by the spark plug and the high voltage terminal of the transformer.

For safety reasons as well as convenience, the ignition transformer was mounted on the rear of the cabinet with the high voltage terminals on the inside. A switch is located in the primary circuit and placed so that it is actuated by the opening and closing of the cabinet door. Its use makes it impossible to turn on the high voltage current when the door is open. In fastening the transformer to the cabinet, the midpoint of the high voltage winding was grounded and the circuit was completed to the burner rim. Only half of the high voltage winding is utilized, since the voltage is sufficient to furnish the desired spark.

A convenience when making adjustments to the burner or gas supply is to turn the timer to focus, which bypasses the timer and holds the solenoid open for a steady flame.

With this arrangement, the procedure for exposing the fabric in the vertical test is essentially as given below. After the gas supply and burner have been adjusted as prescribed, the flame is extinguished and a normally prepared specimen is suspended in the usual manner. The door is closed, the start button is pressed to start the ignition spark, the solenoid valve is opened, and the timing of the cycle is begun. The start button is released as soon as the gas has ignited. The remainder of the procedure is identical with the usual methods, except that the gas is automatically shut off at the end of the predetermined period.

The arrangement described above has been in use for several years at this laboratory and has been found practical, simple to use, and troublefree. The results obtained with it are viewed with greater confidence because of the better control of the exposure interval and the undivided operator attention to timing the after-flame and after-glow in the fabric.

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JOHN D. TALLANT

Fiber Crystallinity During Acid Hydrolysis

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June 24, 1957

To the Editor
Textile Research Journal

Dear Sir:

It has been reported by several workers [2, 4, 5, 7, 9, 12] that during the mild heterogeneous acid hydrolysis of cellulosic fibers the breaking of the chains in the accessible region allows the broken chain ends freedom to rotate; under the plasticizing influence of both heat and water they tend to extend the already formed crystallites. The concept of fiber crystallization during mild hydrolysis was supported by the results of fiber crystallinity measurements by X-ray diffraction techniques [8], fiber density determinations [3, 10, 11], and moisture regain values of the hydrolyzed products [5, 7]. However, very little information is available regarding changes in the crystalline fraction of different cellulosic fibers when subjected to identical conditions of mild acid action; therefore, it was thought desirable to study these changes for a variety of cellulosic fibers. The method of estimation of crystalline fraction in cellulosic fibers suggested by Hessler and Power [6] proved to be a convenient technique for the present work.

Sulfuric acid was used as a hydrolyzing agent because the hydrolytic conditions were less severe and the reaction could be better controlled than with other agents. Standard cellulose prepared from Indian cotton, standard cellulose mercerized with 18% caustic soda at 15° C. with and without the application of tension, viscose rayon, and cuprammonium rayon were used as fiber substances. Hydrolysis of all the fibers was carried out using 6 N H_2SO_4 at $30 \pm 1°$ C. for different periods, keeping the liquor/material ratio at 50/1. After hydrolysis, the samples were washed free of acid with distilled water, air dried, and brought to equilibrium moisture content at 65% R.H. and 30° C. The loss in weight sustained by the fiber substance during the various stages of hydrolysis was determined. Basic D.P. of the conditioned samples was determined from viscometric measurements of standard cuprammonium hydroxide solutions containing the samples by the method suggested by Battista [1]; the fiber crystallinity was obtained from the iodine adsorption measurements [6]. Results are given in Tables I and II and Figure 1.

Results of the present work indicate that in the initial stages of acid hydrolysis the noncrystalline regions, consisting of disordered portions of cellulose chains characterized by almost complete accessibility, are progressively removed; simultaneously the fine structure of cellulose undergoes crystallization. With all the fibers studied, the increase in fiber crystallinity is much more than can be accounted for by the weight loss the fiber substance has suffered during the acid action. This indicates clearly that positive crystallization of cellulose chains does take place with progressive removal of the accessible region in the initial stages of acid action. The crystalline fraction in the fiber substance increases rapidly in the initial stages, but after a definite loss in the fiber substance has taken place no further crystallization occurs. The final values of the crystalline fraction after hydrolysis are the same for cellulose mercerized both with and without tension (86%) and for the two regenerated fibers (81–82%). The total increase in fiber crystallinity with progressive loss in weight of the fiber substance increases in the following order: standard cellulose < cellulose mercerized with tension < cellulose mercerized without

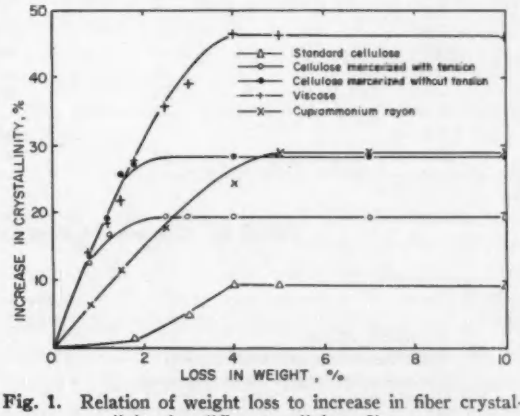

Fig. 1. Relation of weight loss to increase in fiber crystallinity for different cellulose fibers.

tension < cuprammonium rayon < viscose rayon. Further, the stage at which increase in the crystalline fraction comes to a standstill is different for different fibers. For instance, with cellulose mercerized with or without tension, after a weight loss of only 2.5% there is no further increase in the fiber crystallinity, whereas in the case of standard cellulose, viscose rayon, and cuprammonium rayon, the constant value for crystalline fraction is obtained after the fiber substance has suffered a loss of about 3.5, 4, and 5% respectively. In the very initial stages of acid action, i.e., for weight losses below 1%, the rate of increase of the crystalline fraction is nearly the same for cellulose mercerized with and without tension and for viscose rayon. Similar to the observations recorded by Howsmon [7] the major part of the increase in crystallinity with most of the cellulosic fibers occurs with a loss in weight of about 1.5–2%. In case of standard cellulose the rate of increase as well as the total increase in the crystalline fraction is not very considerable, while with mercerized fibers and regenerated fibers both the rate of increase and the total increase in crystallinity are quite appreciable. During mercerization, because of the action of caustic soda, the original crystal structure is disrupted and the original network of crystallite is changed to a new one with much shorter periodicity. In the case of regenerated fibers, disruption of the original crystal structure and reformation of a new one takes place during the dissolution of cellulose in the solvent and subsequent coagulation in the spinning bath respectively. The changes in the crystal structure have been shown to be more pronounced with regenerated cellulosic fibers than with mercerized celluloses. In both these cases two chains may be trapped in two different crystal nuclei with different lengths of each chain between these points of crystallization. During the acid action, chain rupture takes place with the result that the strain induced by crystallization is relieved and the loose chain ends become free to move. This allows considerable crystal growth to take place along the chains.

Another interesting observation recorded is that with all the cellulosic fibers examined, the increase in fiber crystallinity ceases at the same stage (as indicated by weight losses) where the leveling of D.P. takes place (Table II). It is very likely that when

TABLE I. Effect of Acid Hydrolysis on Cellulose Fiber Crystallinity

% Loss in weight	% Crystalline fraction				
	Standard cellulose	Cellulose mercerized under tension	Cellulose mercerized without tension	Viscose rayon	Cupram-monium rayon
nil	86	72	67	56	62
0.8	—	81	76	63	66
1.2	—	84	80	66	—
1.5	—	—	84	68	69
1.8	87	—	85	71	—
2.5	—	86	—	76	73
3.0	90	86	—	78	—
4.0	94	86	86	82	77
5.0	94	—	—	82	81
7.0	—	86	86	—	81
10.0	94	86	86	82	81

TABLE II. Changes in D.P. of Cellulose Fibers During Acid Hydrolysis

	Initial D.P.	Leveling off D.P.	% Loss in wt. corresponding to leveling off D.P.
Standard cellulose	2230	350	4.0
Cellulose mercerized with tension	1850	220	2.5
Cellulose mercerized without tension	1660	200	2.7
Viscose rayon	445	150	4.5
Cuprammonium rayon	600	160	4.8

the splitting of the long chain molecules comes to an end, as indicated by the leveling of D.P., no further segmental rearrangement is possible; therefore further crystallization is not observed after this stage of acid action.

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E. H. Daruwalla
P. Subramaniam

A New Approach to the Determination of the Accessibility of Wool to Sorbates

Wool Textile Research Laboratory
Commonwealth Scientific and
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Geelong, Australia
May 20, 1957

To the Editor
Textile Research Journal

Dear Sir:

The accessibility of wool toward sorbates is a matter of importance for two reasons. The first is that the chemist is frequently concerned with reactions of specific groups on the fiber, either with a view to estimation of that group, as in end group analysis, or masking its effect in the wool molecule by complete substitution. It often happens that the desired reaction does not proceed to completion; this is usually attributed to inaccessibility of specific groups of the wool fiber toward the reagent. The second reason is that the accessibility of the fiber to small molecules is related to its crystallinity, as observed by X-ray studies. It is the purpose of this letter to discuss the sorption isotherm method of measuring accessibility and to propose a new approach based on measurement of the empty space within the fiber which is occupied by the sorbate at saturation regain.

From a theoretical analysis of the sorption isotherm for a fiber, Hailwood and Horrobin [5], using the experimental data for a number of different fibers in water, calculated the fraction of the fiber accessible to the sorbate. The derivation of the isotherm is based on a model in which the sorbate is assumed to exist in two states; (i) in simple solution, and (ii) combined to form a hydrate with a definite unit of the fiber molecule. It is assumed that the system is an ideal solution of the anhydrous fiber, hydrated fiber, and water. This assumption of ideality has been criticized severely by Cassie [3], Gee [4], and Barrer [1].

The theoretical equation describing the isotherm has the form

$$A + Bh - Ch^2 = h/r$$

where h is the relative humidity, r the regain, and A, B, and C are constants, which can be suitably chosen to fit closely any S-shaped isotherm. The constant A is related to a quantity M, which is defined as the "molecular weight" of that unit of the fiber molecule which combines with one molecule of sorbate. In all cases it is found that the calculated value of M is considerably greater than the mean

residue weight R of the fiber, which is the average weight of the unit containing one polar group capable of bonding with a water molecule. Hailwood and Horrobin [5] suggested that this difference is due to the inaccessibility toward water of some sites in the fiber, and used the ratio R/M as a measure of the accessibility of the fiber to water. In this way they obtained an average value of 0.55 for the accessibility of the wool fiber to water, whereas Nicholls and Speakman [11] obtained values ranging from 0.63 to 0.70. However, the latter authors state [11, 13] that these values should not be taken too seriously, in view of an apparently anomalous result with methylated Lincoln wool and the results obtained by an independent method [2].

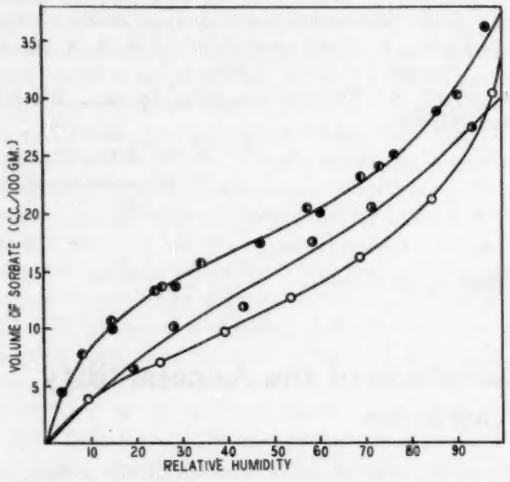

Fig. 1. The sorption isotherms at 25° for water, ○; methanol, ●; ethanol, ◐, and n-propanol, ◑; from the results of Nicholls and Speakman [10].

In the application of the Hailwood-Horrobin treatment to water and the lower primary alcohols, Nicholls and Speakman [10] make the tacit assumption that the molecules, irrespective of their size, should be able to attach themselves to neighboring polar groups on the wool with equal facility. However, it is clear that one would expect more steric interference between two n-propanol molecules (each of molecular volume 125^3 Å) attached to neighboring sites than between two water molecules (each of molecular volume only 30^3 Å).

Such steric effects would cause a progressive decrease of the molar sorption as the size of the alcohol increases. This has been observed by Nicholls and Speakman [10] and attributed by them to decreasing accessibility, whereas in actual fact approximately the same volume of sorbate has been sorbed in each case at saturation (see Table I and Figure

TABLE I. Summary of Saturation Sorption Data on Wool at 25°

	Water	Methanol	Ethanol	n-Propanol	Reference number
Regain (g. sorbate/g. wool)	0.33	0.26_2	0.21_3†		7
	0.34*	0.28_7*	0.24_4*	0.03_3*†	12
	0.33	0.28	0.26	0.20†	8
	0.32_6**	0.33_3**	0.28**	0.25**	9, 10
Mean value	$0.33_2 \pm .003$	$0.29_2 \pm .016$	$0.26_1 \pm .010$	0.25	
Volume sorbed (cc./g. wool)††	0.33_2	0.37_1	0.33_2	0.31_3	
Volume swelling (cc./cc. wool)		0.40_9‡	0.36_8‡		7
		0.38	0.33		8
	0.36_8				14
Mean value	$0.36_8 \pm .007$	$0.39_5 \pm .015$	$0.34_9 \pm .019$		
Volume swelling (cc./g. wool)	0.28_2	0.30_2	0.26_8		
Volume of empty space in wool occupied by sorbate (cc./g. wool)	$0.05 \pm .010$	$0.068 \pm .031$	$0.065 \pm .029$		

* Measurements made at 22.2° C.

† Results are low because insufficient time was allowed for equilibrium to be attained. Methanol, ethanol, and n-propanol require 2–4 days, 3–5 weeks, and 3–6 months respectively [10].

** Extrapolated values.

†† Calculated on the assumption that sorption occurs without change of density of the sorbate.

‡ Calculated from King's density data using the mean values of regain shown in Table I.

1). In Table I it is shown that at saturation there is approximately the same volume swelling for water, methanol, and ethanol (no figures are available for n-propanol); hence the same volume of empty space [6] in the wool fiber is filled by these sorbates at saturation. It is therefore reasonable to suppose that wool is equally accessible to water, methanol, ethanol, and probably n-propanol.

It may be possible to measure the relative accessibility of wool towards various sorbates by calculating the volume of empty space occupied by the sorbates in the wool at saturation. As shown in Table I, this involves the accurate determination of the regain and volume swelling at saturation; *e.g.*, in the case of water a 1% error in their measurement leads to a 12% error in the volume of empty space. It also involves the reasonable assumption that sorption occurs without change of density of the sorbate [6]; experiments are in progress to test the possibilities of this method.

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J. H. BRADBURY

Book Reviews

The Chemistry of Petrochemicals. Melvin J. Astle. Reinhold Publishing Corp., New York, 1956. 267 pages. Price $6.50.

Reviewed by Lorence Rapoport, American Cyanamid Company, Stamford Research Laboratories, Stamford, Conn.

This book presents an up-to-date survey of the many facets of the burgeoning petrochemical industry. This industry has grown since its origin in the early 1920's to the present situation where well over 50% (by value) of all chemicals produced in the United States can be classified as petrochemicals. The author has used the now generally accepted convention of designating a petrochemical as one manufactured from petroleum or natural gas sources.

In systematic fashion, the author considers the sources of the various hydrocarbons derived from petroleum and then discusses the chemical processes by which they are converted into industrially important commodities. Thus the Fischer-Tropsch and related processes as supplements to the naturally occurring paraffin hydrocarbons are treated first, followed by a chapter on the reactions of the paraffin hydrocarbons. There follows a brief discussion of the preparation of olefins via cracking and dehydrogenation processes, after which the utilization of olefins in the commercially important halogenation, hydration, oxidation, and oxo reactions is considered. The polymerization and alkylation reactions of olefins are treated, after which there is a short chapter on diolefins. The preparation of acetylene from natural gas and a short survey of some of its more important reactions are discussed next. Following a brief chapter on the cyclic paraffins, there is a discussion of the aromatic hydrocarbons, whose origin from petroleum sources is of increasing importance. In the concluding chapters various classes of compounds ultimately derived from petroleum hydrocarbons are discussed. These include olefin oxides, alcohols, aldehydes and ketones, acids, amines, and nitriles.

The book on the whole is well written and relatively free from the inevitable errors which survive through to print. Detailed reaction conditions for many processes are presented, but in some instances

these are taken from patent examples, and may not be representative of those employed in actual practice. This book will be of more interest and value to the reader who desires a broad survey of the field of petrochemicals than to the research-scientist active in the field. As such it should be of considerable utility for college courses in industrial chemistry.

Asbestos: From Rock to Fabric. Charles Z. Carroll-Porczynski. The Textile Institute, Manchester, England, 1956. 415 pages. Price 55/ ($7.75).

The subtitle "From Rock to Fabric" is definitive of the contents of the book, which is the most comprehensive treatment published to date. The early chapters have to do with asbestos minerology, physical and chemical properties, mining methods, and methods of extraction from the rock. In these chapters the different types of fiber are described, accompanied by fiber photomicrographs, and the principal sources given. Methods of manufacture of asbestos products from blending of fibers through carding, spinning, and weaving are covered in some detail followed by a chapter on asbestos textiles and chapters on the use of asbestos in brake linings, in the plastics industry, and other industrial uses. Test methods are described. Summaries of important patents are included and the chapters are well documented by references. Because of the fact that published information on asbestos is relatively scarce and somewhat scattered, this book will be found valuable for reference purposes.

Natural and Synthetic Fibers Yearbook 1955. Edited by Milton Harris and H. Mark. Interscience Publishers, Inc., New York, 1956. 950 pages. Price $45.00.

This volume comprises the abstracts originally published monthly during 1955, in loose-leaf form, for subscribers to the Interscience Textile Abstract Service. These abstracts differ from the conventional abstracts in that they are far more complete and generally contain original data, graphs, charts, photographs, etc. Essentially they are digests which furnish sufficient information so that in many cases it is not necessary for a researcher to refer to the original article.

Articles to be abstracted are selected from the outstanding world publications and represent current progress in textiles throughout the world. The digests, in English, of articles which have appeared in foreign language publications will be particularly useful to many investigators. The bound and indexed volume makes the information easily accessible in libraries for reference purposes.

Latex: Natural and Synthetic. Philip G. Cook. Reinhold Publishing Corp., New York, 1956. 231 pages. Price $3.50.

Reviewed by D. W. Peabody, Research Division, Goodyear Tire and Rubber Co.

This is one of the Reinhold Pilot Books Series. These books are designed to contain all essential material, and yet be short, and written in a language understandable to one who is not an expert. "Latex: Natural and Synthetic" carries out this idea very well. It is amazingly complete, giving a good picture of the history, uses, testing, and processing of natural and synthetic rubber latices. It covers the uses of latex in coating, impregnating, and backing of fabrics of various kinds.

It is an invaluable book for someone new in the latex field and very helpful for those already engaged in latex work.

It is well indexed and contains useful diagrams and a good bibliography so that more details on any phase may be found.